Comparison of SiON layers doped with phosphorous and boron for integrated optics applications

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In this work plasma enhanced chemical vapor deposition (PECVD) were adopted to achieve boron/phosphorous (B/P) doped silicon oxynitride (SiON) layers. By adjusting the flow rates of corresponding gas precursor (PH_3/Ar or B_2H_6/Ar), SiON layers with different B or P concentrations were obtained. Measurements by X-ray photoelectron spectroscopy (XPS) have shown that PH_3 can result in more efficient doping in the layers than B_2H_6. Compared with B-doped samples, reduction of the hydrogen content can be more easily observed in P-doped SiON layers, as been confirmed by Fourier transform infrared spectroscopy. Hydrogen-related chemical bonds became undetectable after annealing of samples at temperatures as low as 700˚C. These results are quite helpful to further research on B/P co-doped SiON layers in application of integrated optical waveguide devices.

Introduction

Silicon oxynitride (SiON) is a very competent candidate material for integrated optics thanks to its excellent properties such as low loss, design flexibility and high thermal stability [1-2]. Growth of SiON layer can be realized by CMOS-compatible chemical vapor deposition (CVD) technologies. However, due to the introduction of hydrogen-containing precursors, as-deposited SiON layers may show hydrogen-related loss properties, especially in wavelength window for telecommunication application [3-4]. Although the influence of hydrogen can be eliminated under the help of high temperature annealing, the necessary annealing temperature for pure SiON is unfortunately as high as 1100˚C so that many side effects such as film cracking and interface diffusion will become prominent [2], which has been a big technical challenge in this research field.

By the introduction of boron (B) and phosphorous (P) into the SiON layers, the above-mentioned research challenges can be alleviated. In this paper, B/P doped SiON layers with different B/P concentrations were deposited, followed by annealing of the samples at varied temperatures. The properties of the as-deposited and annealed layers were characterized and the results of the measurements were discussed.

Experiment details

Plasma enhanced chemical vapor deposition (PECVD) process was adopted for the fabrication of the SiON layers for the presented study. 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). 2% SiH_4/N_2 (Silane diluted in N_2) and N_2O served as gas precursors for the deposition of undoped SiON layer, while B-doped and P-doped samples were realized by the introduction of 5% B_2H_6/Ar (diborane diluted in Ar) and 5% PH_3/Ar (phosphine diluted in Ar) with varying flow rates into the deposition process. The deposition time for each sample was adjusted

such that the thicknesses of all achieved layers are around 1 micron for convenience of comparison. X-ray photoelectron spectroscopy (XPS) was used for the measurements of element concentrations within the layers.

After deposition, all the samples were annealed in N_2 ambient for 3 hours. The annealing temperatures vary from 600˚C to 1100˚C. The refractive indices and chemical bond information of the as-deposited and the annealed samples were characterized by spectroscopic ellipsometry and Fourier Transform Infrared (FTIR) spectroscopy, respectively.

Characterizations and discussions

Concentration of dopants

For easy comparison of the B/P concentration in the doped SiON layers, two as-deposited samples B40 (40sccm flow rate of 5% B_2H_6/Ar) and P40 (20sccm flow rate of 5% PH_3/Ar) was measured by XPS. The results showed that the concentration of B in B40 (6.39 atom %) was lower than that of P in P40 (7.17 atom %). Considering the fact that there are two B atoms in B_2H_6 while only one P atom in PH_3, such a conclusion may be drawn that phosphorous can be incorporated into SiON layers more efficiently than boron in our present deposition.

Refractive index changes

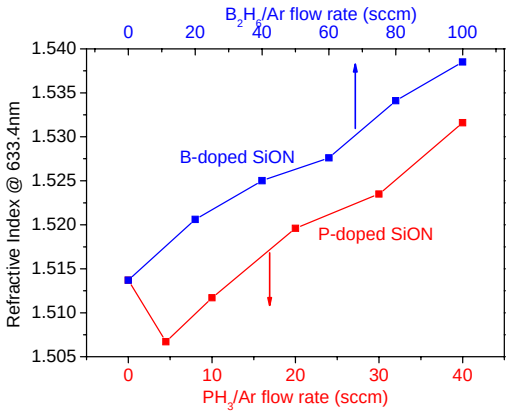
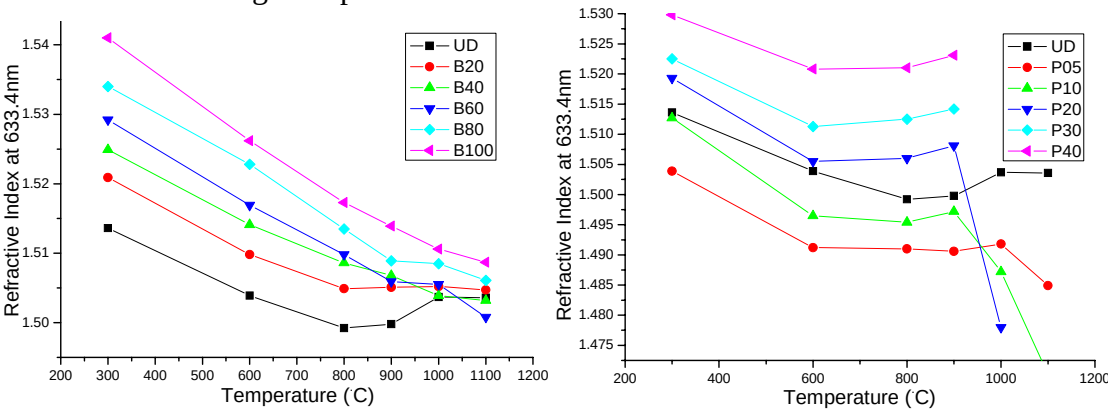


Figure 1. Refractive indices of as-deposited layers as a function of the B_2H_6/Ar and PH_3/Ar flow rates

Figure 1 shows the refractive indices of the as-deposited samples. As is well-known, the refractive index of BPSG increases with the concentration of phosphorous while it decreases with that of boron. Therefore, the refractive indexes of B/P-doped SiON layers are expected to vary in a similar way. However, the measurements showed that the refractive indices of B-doped SiON layers vary towards the opposite direction. For P-doped SiON layers, no monotonous change of the refractive index with PH_3/Ar flow rate was observed and a minimum of refractive index was measured when PH_3/Ar = 5sccm (Fig. 1). These phenomena can probably be attributed to the changes of elemental concentrations in the layers and the variation of layer densities, which needs further investigations.

The relations between refractive indices of all the samples and the annealing temperatures are shown in Figure 2. As can be seen, for undoped sample (UD), its refractive index decreased with the increase of temperature until a minimum at 800˚C

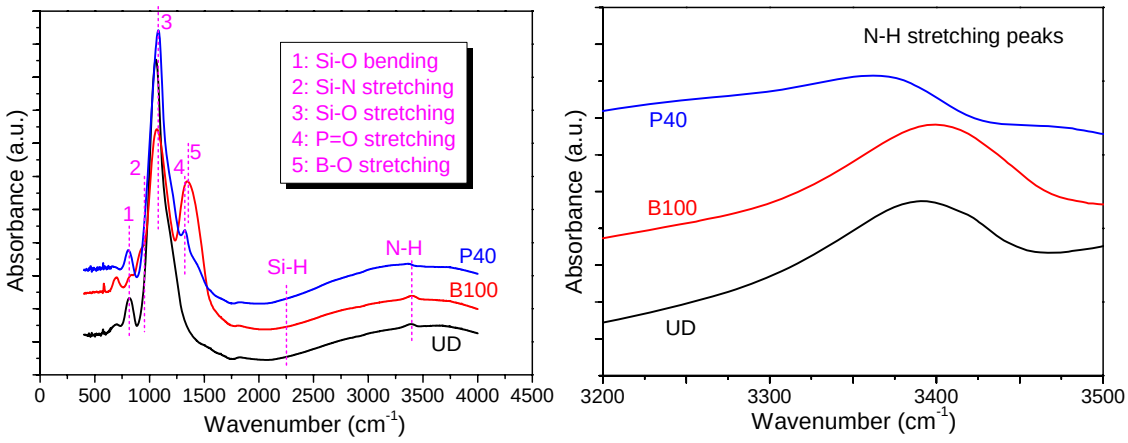
was reached, followed by a slightly increase afterwards. For the B-doped samples, however, the refractive indices decreased monotonously (Figure 2(a)), and the index changes increased with flow rates of B_2H_6 (and expectedly the concentration of B in the layers). For P-doped SiON layers, similar changes of refractive index to that of the undoped sample were observed, as shown in Figure 2(b). However, when the annealing temperature went to 1000˚C and higher, samples with high P concentrations (P30 and P40 in our case) became opaque and could not be measured any more. Scanning electron microscopy (SEM) showed that air voids were formed in the layer, which could be attributed to the formation of P_2O_5 clusters within the layers and their violent boiling or sublimation at high temperatures.



(a) (b)

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

Hydrogen reduction in SiON layers



(a) (b)

Figure 3. (a) Comparison of full FTIR spectra of three as-deposited samples; with indication of the positions of some absorption peaks under our interests, (b) Magnification of spectral section containing the absorption peaks caused by stretching of N-H bonds

The FTIR spectra of three as-deposited samples (UD, B100 and P40) were shown in Figure 3, where vertical offsets were introduced to different curves for clarity and ease of comparison. No Si-H peaks (around 2250cm^{-1}) were observed in all the samples. The absorbance peak attributed to stretching of N-H bonds (around 3350cm^{-1}) can be clearly seen in Figure 3(b). Compared to the pronounced N-H peak in undoped sample, a significant reduction of N-H bonds in P-doped SiON layers has been detected. In B-doped samples, however, no obvious changes were observed.

Further reduction of N-H peaks can be achieved by annealing treatments, as shown in Figure 4. With the increase of annealing temperature, the reduction of N-H bonds can be observed even in the undoped sample (UD) (Figure 4(a)). More obvious decrease of the N-H absorption peak was measured in B-doped sample. In B100 case specifically, N-H peak went below detection limit of FTIR when an annealing temperature as high as 900˚C was applied (Figure 4(b)). Furthermore, complete elimination of the N-H bonds could be more easily achieved in P-doped samples. In P40 case for example, the N-H peak disappeared even when the samples was treated at temperature as low as 700˚C (Figure 4(c)).

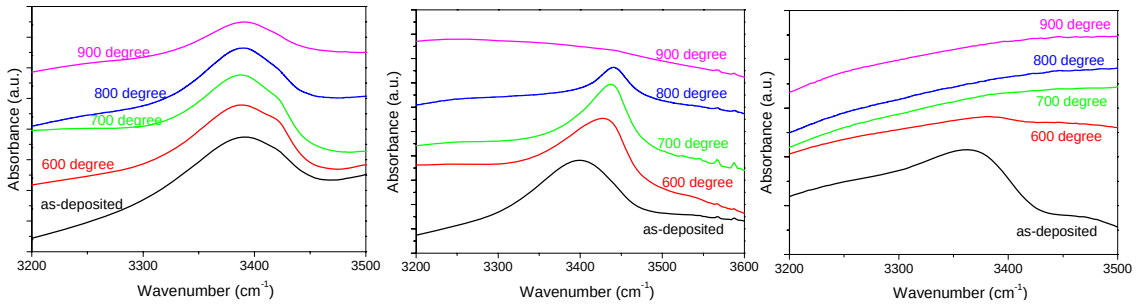


Figure 4 Reduction of N-H absorption peaks upon anneal treatment at varied temperatures: (a) undoped sample UD, (b) B-doped sample B100, and (c) P-doped sample P40

Conclusion

Plasma enhanced chemical vapor deposition was adopted for the preparation of B-doped and P-doped SiON layers by introduction of 5% PH_3/Ar and 5% B_2H_6/Ar into the growth process. XPS measurements showed that doping of phosphorous into the layer is more efficient than the incorporation of boron. After annealing treatment, the refractive indices of B-doped samples decrease with the increase of annealing temperature. The variation curves between refractive indices and annealing temperatures in P-doped samples bore more similarities to that of the undoped layer. However, when the annealing temperature goes above 900˚C, violent boiling or sublimation of P_2O_5 clusters within the layers will result in disasters in the layers. FTIR measurements have shown that sufficient removal of N-H bonds can be achieved at an annealing temperature as low as 900˚C in B-doped SiON layers. In P-doped cases, this temperature can be further reduced to 700˚C. Therefore, phosphorous plays a leading role in the reduction of hydrogen in SiON layers.

References

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