

Reduction of N-H Absorption Peaks by B or P Doping of PECVD SiON Layers for Integrated Optics

F. Sun, A. Driessen, and K. Wörhoff

Integrated Optical MicroSystems Group, MESA+ Institute for Nanotechnology,
University of Twente, Enschede, The Netherlands
F.Sun@ewi.utwente.nl

Abstract—Boron or Phosphorous doped PECVD silicon oxynitride layers were fabricated and thermally treated. From the FTIR absorption spectra of the layers, N-H concentrations were obtained as functions of dopant concentration and annealing temperature. Significant reduction of N-H bonds has been observed after annealing at a temperature as low as 700°C.

Keywords- Silicon oxynitride, integrated optics, boron and phosphorus doping

I. INTRODUCTION

The excellent properties of silicon oxynitride (SiON), such as high transparency, adjustable refractive index and good stability, add to the attractiveness of this amorphous material for application in integrated optics [1-4]. High-quality SiON layers are reliably grown by chemical vapor deposition (CVD). However, the hydrogen-containing precursors applied in the deposition processes will inevitably lead to incorporation of hydrogen (H) bonds (Si-H, N-H, O-H) into the as-deposited SiON films. Those bonds, are well-known to cause absorption peaks at wavelength ranges around 1.5 μm [3, 4]. Annealing at high temperature ($>1100^\circ\text{C}$) can be applied to reduce the H-content and to achieve SiON-based optical waveguides with low loss [2, 3]. However, the high temperature required for sufficient hydrogen removal induces several undesired side effects such as inter-layer diffusion and micro-cracks [3].

The above problems can be addressed by introducing boron (B) and/or phosphorous (P) into the layers. Because of the weakening of chemical bonds induced by the dopants within the layers, the hydrogen bond formation will be suppressed, and annealing at lower temperatures is sufficient for further H reduction.

In our study, 5% $\text{B}_2\text{H}_6/\text{Ar}$ and 5% PH_3/Ar were added into the gas precursors of plasma enhanced (PE) CVD processes, in order to fabricate B and P-doped SiON layers, respectively. The samples were annealed in nitrogen ambient at temperatures varying from 600-900°C. The H-bond concentrations were measured by Fourier transform infrared (FTIR) spectroscopy.

II. CHARACTERIZATION

In Fig. 1 the full FTIR spectrum of a SiON layer is shown including the positions of the absorption peaks corresponding to the three H bonds. In the FTIR spectra of all the samples, no Si-H peaks were observed within the detection limit, while the

N-H peaks dominate the O-H peaks, as can be seen from the inset of Fig. 1. Therefore we only consider the change of N-H peaks for simplicity. The concentration of N-H bonds can be calculated by the method of Lanford and Rand [5].

Detailed analysis showed that the N-H absorption peak can be deconvoluted into two symmetric Gaussian peaks, noted as NH1 and NH2 (inset of Fig. 1). Peak NH1 is the contribution from the stretching of N-H...N, the bonding between the H atom in N-H bond and the lone pair electrons of another N atom nearby [6]. Compared to normal N-H stretching modes (NH2 peak), the NH1 peak is significantly broader and shifts to lower vibration frequencies.

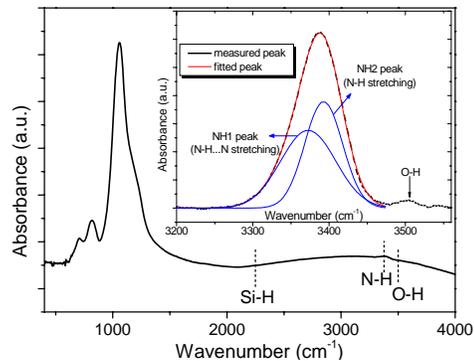


Figure 1. FTIR spectrum of SiON layer with indication of the absorption peak positions corresponding to Si-H stretching, N-H stretching and O-H stretching. (The inset shows details of N-H and O-H absorption peaks after baseline correction, where the N-H peak is deconvoluted into two Gaussian peaks)

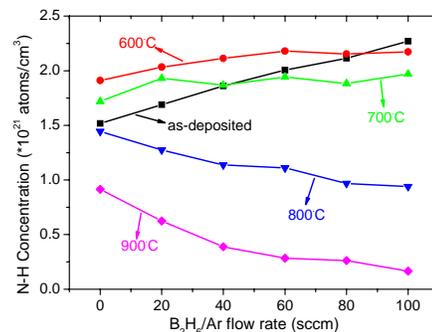


Figure 2. N-H concentration changes with annealing temperature and flow rates of gas precursors in B-doped SiON layers

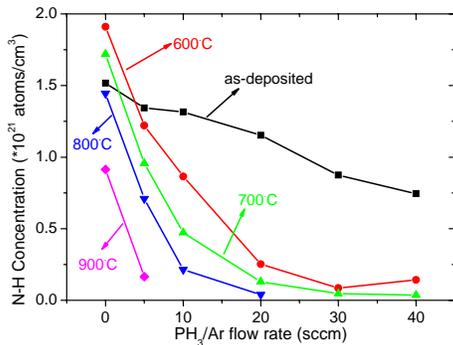


Figure 3. N-H concentration changes with annealing temperature and flow rates of gas precursors in P-doped SiON layers

III. DISCUSSION

The influences of the annealing temperature and the dopant gas flow rates on the N-H-bond concentration are shown in Fig. 2 and Fig. 3. As can be seen in Fig. 2, in as-deposited B-doped SiON, the N-H concentration increases with the B_2H_6/Ar flow rate. There is no monotonous correlation between N-H concentrations and annealing temperatures. In undoped layers as well as in most of the B-doped layers, the N-H concentration first increases slightly with annealing temperature, followed by significant N-H reduction when the temperature increases further. The efficiency of N-H removal by annealing increases with the flow rate of B_2H_6/Ar . In sample B100 ($B_2H_6/Ar=100$ sccm), for example, the highest N-H concentration among all the as-deposited B-doped layers was measured, while these N-H bonds are easiest to be eliminated by thermal treatment. After annealing at $800^\circ C$, B100 presents the lowest N-H concentration. More significant N-H reduction was observed in P-doped SiON layers. As shown in Fig. 3, the N-H concentration decreases not only at higher PH_3/Ar flow rate, but also more rapidly with the increase of annealing temperature. The N-H reduction in P-doped samples is highly efficient; in layers grown at higher PH_3/Ar flow rates and/or annealed at higher temperatures, the N-H peak decreases below the detection limit and can not be observed in the FTIR spectra. In sample P40 ($PH_3/Ar=40$ sccm), for example, the N-H concentration decreases to a level very close to the detection limit after annealing at $700^\circ C$, and can not be detected any more after further increase of the temperature.

Based on the deconvolution of N-H absorption peaks in the FTIR spectra of all samples, further investigations on the concentration variations of N-H...N bonds and normal N-H bonds, corresponding to NH1 and NH2 peaks in the inset of Fig. 1, were carried out. Fig. 4 presents the concentration change of NH1 and NH2 with annealing temperature in three samples. In the undoped layer (UD), the concentrations of N-H...N bonds and normal N-H bonds have similar variation trends with temperature and remain approximately the same in both as-deposited and annealed films. In B-doped SiON layers, the initial increase of N-H...N concentration with annealing temperature is more prominent than that of normal N-H bonds, followed by a more rapid N-H...N bonds elimination with further increase of temperature. Thus the N-H...N bonds can

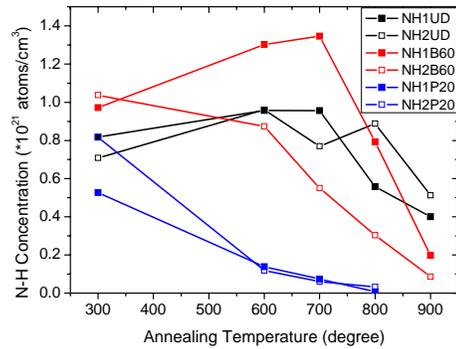


Figure 4. NH1 and NH2 concentration changes as a function of annealing temperature in undoped, B60 and P20 samples

dominate N-H bonds at moderate annealing temperatures. In P-doped SiON layers, however, normal N-H bonds are more preferable than N-H...N bonds in as-deposited films. After annealing, the concentration of these two types of bonds becomes almost identical.

IV. CONCLUSIONS

The concentrations and configurations of N-H bonds in B-doped and P-doped PECVD SiON layers were investigated and discussed. Our analysis showed that N-H bonds can be eliminated more efficiently in P-doped samples. After annealing at a temperature as low as $700^\circ C$, the N-H absorption peak in the FTIR spectra of P-doped SiON films can be reduced to the detection limit. Further study shows that the contribution of N-H...N bonds to the whole N-H absorption peaks varies with annealing temperature and dopant type. More efficient N-H reduction can be expected by means of further improvements on the deposition and annealing processes. Therefore, B- and/or P- doping of SiON films is very promising for the realization of low-loss photonic devices exploiting CVD technology.

REFERENCES

- [1] O. P. Agnihotri, R. Tyagi, and I. Kato, "Silicon oxynitride waveguides for optoelectronic integrated circuits," *Jpn. J. Appl. Phys.*, vol. 36, pp. 6711-6713, November 1997.
- [2] G. L. Bona, R. Germann, and B. J. Offrein, "SiON high-refractive-index waveguide and planar lightwave circuits," *IBM J. Res. & Dev.*, vol. 47, pp. 239-249, March/May 2003.
- [3] K. Wörhoff, A. Driessen, P. V. Lambeck, L. T. H. Hilderink, P. W. C. Linders, and Th. J. A. Popma, "Plasma enhanced chemical vapor deposition silicon oxynitride optimized for application in integrated optics," *Sens. Act.*, vol. 74, pp. 9-12, January 1999.
- [4] F. Ay, and A. Aydinli, "Comparative investigation of hydrogen bonding in silicon based PECVD grown dielectrics for optical waveguides," *Opt. Mat.*, vol. 26, pp. 33-46, January 2004.
- [5] W. A. Lanford, and M. J. Rand, "The Hydrogen Content of Plasma-deposited Silicon Nitride," *J. Appl. Phys.*, vol. 49, pp. 2473-2477, April 1978.
- [6] Z. Yin, and F. W. Smith, "Optical Dielectric Function and Infrared-Absorption of Hydrogenated Amorphous-Silicon Nitride Films: Experimental Results and Effective-Medium-Approximation Analysis," *Physical Review B*, vol. 42, pp. 3666-3675, August 1990.