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Influence of Heat-Treatment Atmosphere on the Bonding and Optical Properties of SiON Films Prepared Using PECVD

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The effects of annealing atmosphere on the Si-O, Si-N, Si-H, and N-H bonding characteristics in SiON films and their structural and optical properties were investigated. X-ray diffractions showed no evidence of crystals in any of the SiON films. The deposition rate increased as the N_2O/SiH_4 flow ratio increased and the SiH_4 flow rate increased. It was possible to obtain SiON films with a surface roughness of about 1 nm and a high deposition rate of about 4 μm/h when the processing parameters were optimized at rf power of 200 W, a N_2O/SiH_4 flow ratio of 3, and a SiH_4 flow rate of 100 sccm. The intensity of Si-O peaks increased in the samples annealed in an oxygen atmosphere, but it decreased in the samples annealed in nitrogen atmosphere. The intensity of the Si-N peak decreased in the samples annealed in an oxygen atmosphere, but it increased in the samples annealed in a nitrogen atmosphere. The position of Si-O peaks shifted from 1030 nm to 1140 nm in the samples annealed both in oxygen and in nitrogen atmospheres. We also observed that the intensities of the Si-H (~2250cm^{-1}) and N-H (~3550cm^{-1}) peaks decreased noticeably as the annealing temperature increased in all annealed samples.

Keywords: SiON, PECVD, planar waveguide

Planar optical waveguides have received great interest in the field of optical communication applications for many years from many companies and universities.[1,2] In the planar optical waveguide, the optically guiding core layer is sandwiched between a lower and an upper cladding layer. Generally, doping with Ge, P, or Ti is done to increase the refractive index of the core layer relative to the cladding layers. The relative difference of the refractive index between the core and the cladding layers is called "index contrast" and is an important parameter for controlling many optical properties of the waveguide.[3] Waveguides with a much higher index contrast are required to decrease the size of a device and to increase the density of devices in a wafer. This has leaded the recent development of new core materials that have high refractive indexes, most notably silicon oxynitride (SiON).[4, 5] The high refractive index contrast waveguide technology based on silicon oxynitride (SiON) makes it possible to fabricate waveguides with considerably higher index contrasts and, thus, a much smaller waveguide bending radii.

The plasma enhanced chemical vapor deposition (PECVD) technique has been used to obtain amorphous non-stoichiometric SiON films from silane and nitrous oxide in recent years.[5] There have been many reports on the preparation of SiON thin films with high deposition rates using PECVD. The fundamental advantage of this technique is that it is easy to control the structural, mechanical, and optical properties of the films deposited by adequately adjusting the deposition parameters.[6-8] However, this technique has the serious problem of remaining Si-H or N-H bonds, which have detrimental effects on the optical properties of the film, remaining inside the film even after the post-annealing process. Therefore, systematic study is needed on the post-annealing effect on the remaining bonding characteristics inside the SiON films.

In this study, we prepared SiON films by PECVD and investigated the basic properties of SiON films, such as refractive indices and the microstructure. In particular, we have focused on the effects of the post-annealing condition that varies by changing the temperature and ambient on the chemical bonding characteristics inside the SiON films.

The SiON films were deposited by the PECVD technique from appropriate gaseous mixtures of silane (10% SiH_4, diluted in N_2) and electronic grade nitrous oxide (99.999% N_2O) in a capacitively coupled reactor. The plasma was activated by a 13.56 MHz radio frequency (rf) signal applied via a matching box to two 400-cm^2 parallel grids. The substrate holder lies 2.35cm below the grids in order to minimize ion-bombardment. All the films were deposited on one-side polished p-type (14-20 ohm cm) silicon (100) wafers. SiON

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Table 1. Parameters for the deposition of SiON films using PECVD

Parameters	Value
RF power (W)	100 ~ 200
SiH_4 flow rate (sccm)	50 ~ 200
N_2O/SiH_4 flow ratio	3 ~ 12
Pressure (torr)	0.2 ~ 0.5

films with different nitrogen, silicon, and oxygen contents were obtained by varying the process parameters such as, N_2O/SiH_4, SiH_4 flow rate, RF power, and working pressure, as shown in Table 1. The deposited samples were annealed at different temperatures (800°C - 1100°C) and in different ambient (Air, N_2, or O_2) for 1 hour.

The crystallinity and microstructure were characterized by X -ray diffraction (XRD) (X'pert-PRO, PHILLIPS, Netherland), scanning electron microscopy (SEM) (S-4700, HITACHI, Japan), and atomic force microscopy (Nanoscope IV, Digital Instrument, USA). A prism coupler (MODEL-1550, Fi-ra, South Korea), having a He-Ne laser at a wavelength of 632.8 nm as a light source, was employed to obtain the thickness and the refractive index of the samples. The compositional and chemical bonding properties of the as-grown and annealed samples were characterized using Fourier transform infrared (FT-IR) spectrometer (NICOLET 520T, Nicolet instrument, USA).

A number of SiON films were grown in this study by changing the varying process parameters, as shown in Table 1. While trying to find the best process condition in which the SiON films can be grown with highest deposition rate and without any artifacts, it was found that the deposition rate strongly depends on the process parameters. The deposition rate increased linearly as the silane flow or rf power increased. Little change in the deposition rate was observed as the N_2O/SiH_4 flow ratio or substrate temperature was changed. The refractive index was also observed to increase linearly as the rf power or N_2O/SiH_4 ratio increased. The refractive index remained almost unchanged as the temperature or silane flow rate were changed. Among these experimental conditions, we selected the optimized experimental conditions for the deposition of SiON thin films to investigate the post-annealing effect. Therefore, SiON films with a refractive index of 1.46798 and a thickness of 3.78 μm were deposited with process parameters of 200 mTorr, 200 W, 350 °C, and a N_2O/SiH_4 flow ratio of 3 in this study.

Figure 1 shows XRD patterns of SiON thin films annealed at various temperatures from 800°C to 1100°C for 1 h in air ambient (a) and a plan-view SEM micrograph of the SiON film annealed at 1100°C for 1h. No diffraction peaks except the Si substrate peak are observed in the XRD pattern, which indicates that SiON films remain in the amorphous phase even after the annealing process. The extremely smooth surface microstructure and lack of contrast difference that

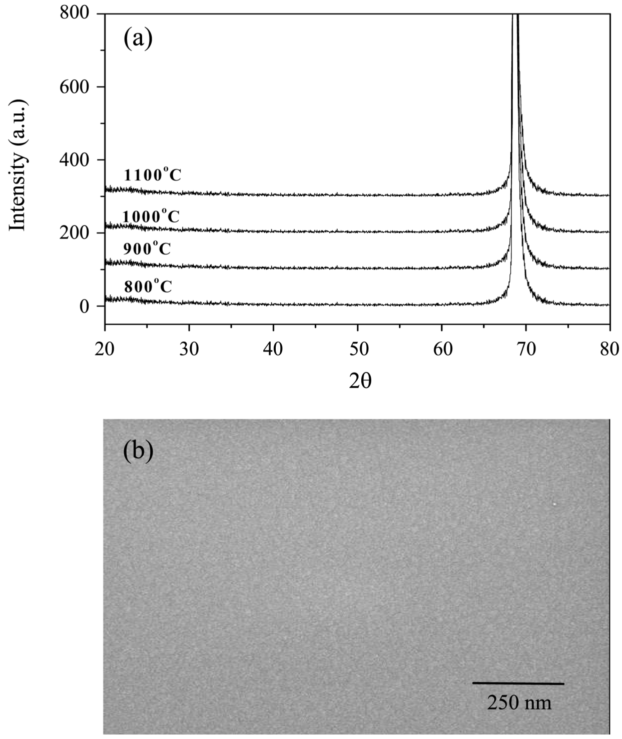

Fig. 1. X-ray diffraction patterns of SiON thin films annealed at various temperatures from 800°C to 1100°C for 1 h in air ambient (a) and a plan-view SEM micrograph of the SiON film annealed at 1100°C for 1 h in O_2 ambient.

shows the microstructural change is observed in the SEM image (Fig. 1(b)). This result is highly consistent with the XRD result.

Magnified FT-IR spectra shows that peaks for the Si-H bonds of the as-deposited SiON film and of the SiON films annealed at different temperatures and in different ambient such as air (a), O_2 (b), and N_2 (c) are shown in Fig. 2. It is clearly observed that the peak intensities of the Si-H bonding in all samples decrease as the annealing temperature increases. It was also observed that the intensity of peaks for N-H bond decreased as the annealing temperature increased (data are not shown here). The effects of the post-annealing conditions on the refractive index of SiON films were also investigated.

Figure 3 shows a change in the refractive index of SiON films, which were annealed in different ambients of O_2 (a) and N_2 (b), as a function of annealing temperature. The refractive index decreases as the annealing temperature increases in all samples. These results are highly consistent with those reported elsewhere.[9] It is interesting to see that there is a difference in the decrease of the refractive index between the SiON film annealed in O_2 ambient and the film annealed in N_2 ambient. The refractive index of SiON films annealed in O_2 ambient decreases from 1.46798 to 1.44968 and that in N_2 ambient drops from 1.46798 to 1.45921. This

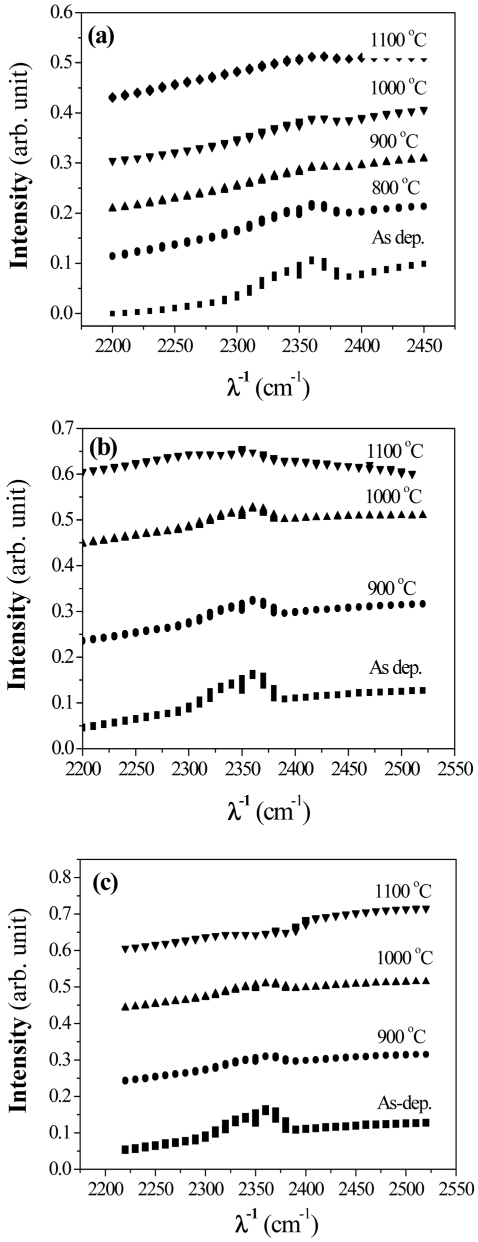

Fig. 2. Magnified FT-IR spectra of the as-deposited SiON film and of SiON films annealed at different temperatures and ambient such as air (a), O_2 (b), and N_2 (c).

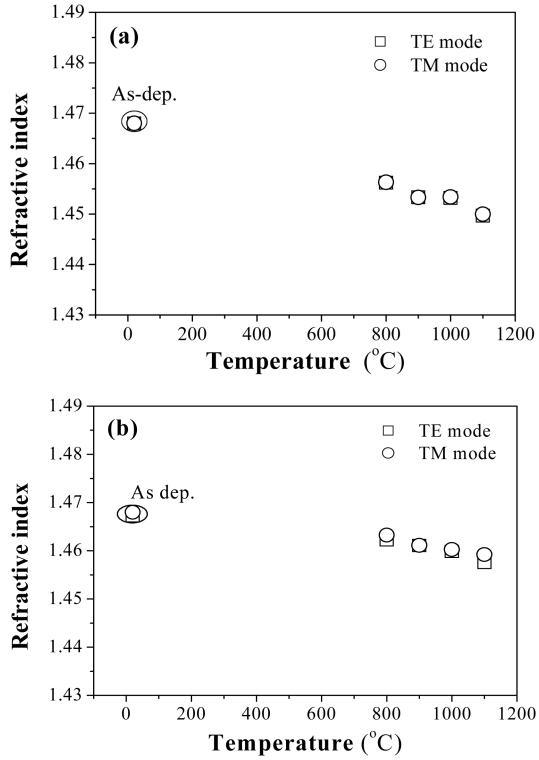

Fig. 3. The change in the refractive index of SiON films, annealed in different ambient of O_2 (a) and N_2 (b), as a function of annealing temperature.

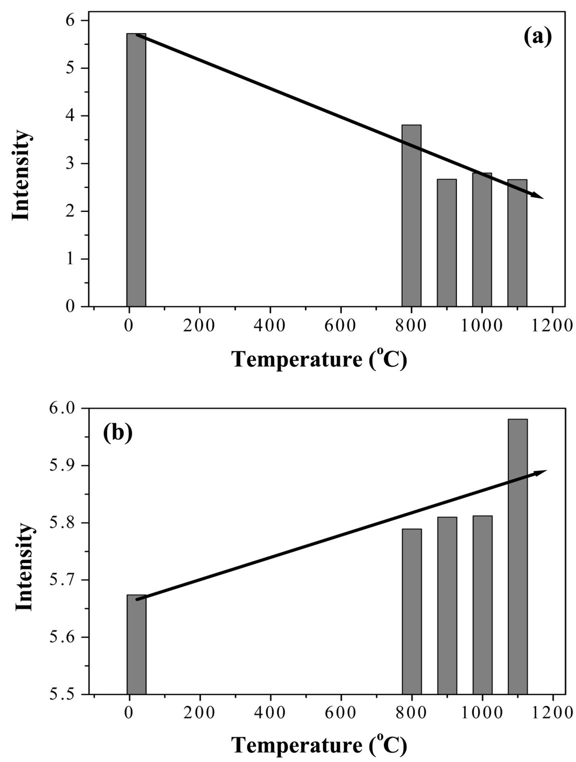

Fig. 4. The intensity change of the Si-O stretching peaks in SiON films, annealed in O_2 ambient (a) and in N_2 ambient (b), as a function of annealing temperature.

result shows that it is more efficient in keeping the refractive index of SiON films to anneal the SiON film in N_2 ambient rather than in O_2 ambient.

We also investigated the intensity change of the Si-O stretching peaks in SiON films annealed in different ambients as a function of annealing temperature because the Si-O stretching peak may cause mechanical stress inside the film.[10] Figure 4 shows the intensity change of the Si-O stretching peaks in SiON films, which were annealed in O_2 ambient (a) and in N_2 ambient (b), as a function of annealing temperature. The intensity values were obtained from the

FT-IR spectra at around 1050cm^{-1}. The intensity of the Si-O stretching peak was observed to increase in SiON films annealed in O_2 ambient, decreasing in N_2 ambient. Details on the relationship between the intensity change of the Si-O stretching peak and the mechanical stress remaining inside the film will be studied further.

In summary, the effects of silicon oxynitride films in different ambients were investigated. Irrespective of the annealing atmosphere, Si-H and N-H bonds disappear with an increase in the annealing temperature (800°C - 1100°C). Also, the refractive index of films annealed at atmospheric pressure in a steam-nitrogen ambient shows more stability than in a steam-oxygen and atmosphere ambient. We guess that the annealing ambient and temperature are highly effective for the mechanical stress of SiON films.

REFERENCES

1. Y. P. Li and C. H. Henry, *IEE Proc. Optoelectron*. **143**, 263 (1996).
2. N. Takato, K. Jinguji, M. Yasu, H. Toba, and M. Kawachi, *IEEE J. Lightwave Technol*. **6**, 1003 (1988).
3. E. Voges, H. Bezzaoui, and M. Hoffmann, *in Proc. 6th Europ. Conf. on Integr. Optics. "ECIO '93,"* (ed., P. Roth), p. 12.4-12.6, CSEM, Neuchatel, Switzerland (1993).
4. H. Albers, L. T. H. Hilderink, E. Szilagyi, F. Paszti, P. V. Lambeck, and Th. J. A. Popma, *in Proc. IEEE lasers and Electro-Optical Society Annual Meeting "LEOS '95"*, **2**, 88 (1995).
5. B. J. Pffrein, G. L. Bona, R. Germann, F. Krommendijk, I. Massarek, and H. W. M. Salemink, *in Proc. Symp. IEEE/LEOS*, (eds., A. Dressen, R. M. de Ridder), p. 290, IEEE, Benelux (1996).
6. C. F. Lin, W. T. Tseng, and M. S. Feng, *J. Appl. Phys*. **37**(Pt. 1), 6364 (1998).
7. C. Dominguez, J. A. Rodriguez, F. J. Munoz, and N. Zine, *Vacuum* **52**, 395 (1999).
8. J. Viard, E. Beche, D. Perarnau, R. Berjoan, and J. Durand, *Journal of the European Ceramic Society,* p. 2025-2028 (1997).
9. Y. T. Kim, S. M. Cho, Y. G. Seo, H. D. Yoon, Y. M. Im, and D. H. Yoon, *Surface and Coatings Technology* **171**, 34 (2003).
10. C. M. M. Denisse, K. Z. Troost, F. H. P. M. Habraken, W. F. van der Weg, and M. Hendriks, *J. Appl. Phys*. **60**, 2543 (1986).