

Characteristics of SiO_xN_y Films Deposited by PECVD at Low-Temperature Using BTBAS- $\text{NH}_3\text{-O}_2$

June Hee LEE,* Chang Hyun JEONG, Jong Tae LIM,

V. A. ZAVALYEV, Kyung Suk MIN, Se Jin KYUNG and Geun Young YEOM[†]

Department of Materials Science & Engineering, Sungkyunkwan University, Suwon 440-746

(Received 27 August 2005, in final form 12 October 2005)

In this study, SiO_xN_y films were deposited at low temperature ($<75^\circ\text{C}$) by inductively coupled plasma chemical vapor deposition (CVD) while biasing the substrate at -80 V using BTBAS/ (O_2/NH_3) . The effects of the oxygen ratio (defined as $\text{O}_2/(\text{O}_2 + \text{NH}_3)$) on the characteristics of the deposited films were investigated. On increasing the oxygen ratio, decreases of C-H and the N-H bonds in the films could be obtained in the deposited SiO_xN_y film while the Si-O bonds increased. Due to low C-H and N-H bond densities in the films with increasing oxygen ratio, the films became more stable, harder, and more transparent. When the oxygen ratio was close to 1, SiO_xN_y resembling SiO_2 with a refractive index of 1.46 was obtained. The oxygen rich SiO_xN_y films produced using $\text{O}_2\text{-BTBAS/Ar}$ are believed to be useful as transparent diffusion barrier materials for the polymeric materials used as organic light-emitting diodes and flexible displays.

PACS numbers: 68

Keywords: PECVD, BTBAS, SiO_xN_y

I. INTRODUCTION

SiO_xN_y films are one of the most widely used in solid state electronic and in optoelectronic devices as insulators and waveguides, and for defect passivation [1-3]. SiO_xN_y films are currently deposited by using physical vapor deposition (PVD), chemical vapor deposition (CVD), or plasma enhanced CVD (PECVD). Of these deposition methods, PECVD allows consistent deposition at low temperatures [4-6].

Bis(tertiary-butylamino)silane (BTBAS) is a chlorine-free organosilicon precursor and a nonpyrophoric stable liquid with a vapor pressure of 6.5 Torr at $40 - 45^\circ\text{C}$ [7]. BTBAS is also safe and easy to handle and has good step coverage compared to other silicon sources, such as SiH_4 , SiH_2Cl_2 , or tetra-ethyl-orthosilicate (TEOS) [7-10]. Recently, BTBAS was studied as a precursor for silicon-nitride, silicon-dioxide, and silicon-oxynitride depositions at relatively low temperatures [7,8].

In this research, the effect of adding a gas mixture of O_2/NH_3 to BTBAS on the physical and chemical properties of SiO_xN_y films, such as the deposition rate, the refractive index, the chemical composition, and the chemical bonding, deposited by a high-density PECVD system was investigated. For future flat-panel-display (FPD)

applications, which may use polymeric films instead of soda-lime glass, a deposition temperature for transparent inorganic films of below 100°C is required so as not to damage the polymer film. Therefore, in this study, the deposition of SiO_xN_y was carried out by using an inductively coupled plasma (ICP) (a high density plasma) at low temperatures without heating the substrate; instead, a bias voltage was applied to the substrate.

II. EXPERIMENTS

Figure 1 shows the schematic diagram of the PECVD system used in this experiment. The plasma source of the high-density PECVD system was a homemade planar ICP source with a three-turn spiral-type copper coil located on the top of the chamber which was made of 10-mm-thick quartz plate. A 13.56-MHz rf power supply was connected to the inductive source while a separate 13.56-MHz rf power supply was connected to the substrate to supply the substrate bias. The substrate was cooled using chilled water; thus, the sample surfaces was kept at $<75^\circ\text{C}$ during biasing so as not to damage the organic-based devices. The details of the plasma system used have been previously described [11].

A combination of $\text{NH}_3\text{-O}_2\text{-BTBAS/Ar}$ was used as the deposition gas. BTBAS is a liquid; therefore, the temperature of the BTBAS bubbler was maintained at 25

*E-mail: omega1234@skku.edu;

[†]E-mail: gyeom@skku.edu; Fax: +82-31-299-6565

°C by using a water bath, and Ar was used as carrier gas. The resulting mix of BTBAS and Ar was passed to the plasma reactor through stainless steel tubing maintained at 80 °C. The reactor was pumped by a booster and rotary pump connected in series, and the total reactive gas flow rate was maintained at 38 sccm (Ar in BTBAS: 8 sccm, O₂ + NH₃: 30 sccm) and the operation pressure was maintained at 80 mTorr. The elemental composition of BTBAS is C₈H₂₂N₂Si; therefore, it was used as a source of silicon and nitrogen; NH₃ supplied the nitrogen, and O₂ removed the CH bonds in the BTBAS and increase the adhesion, hardness, and optical transparency of the deposited SiO_xN_y film.

To determine optimum conditions for SiO_xN_y film for-

mation, are varied the ratio of O₂ to NH₃ from 0 to 1 and investigated the characteristics of the deposited films. The operating conditions used for the deposition of SiO_xN_y are described in Table 1. The thickness of the deposited film was measured using a step profilometer (Tencor Inc. Alpha step 500), and the composition and the chemical bonding states of that film were measured by using X-ray photoelectron spectroscopy (XPS, VG Microtech Inc., ESCA2000) and by Fourier transform infrared spectrometry (FT-IR, Bruker IFS-66/S, Bruker), respectively. The refractive indices of the deposited materials were measured using an ellipsometer (L-117, Gaertner) utilizing a 633-nm He-Ne laser light source.

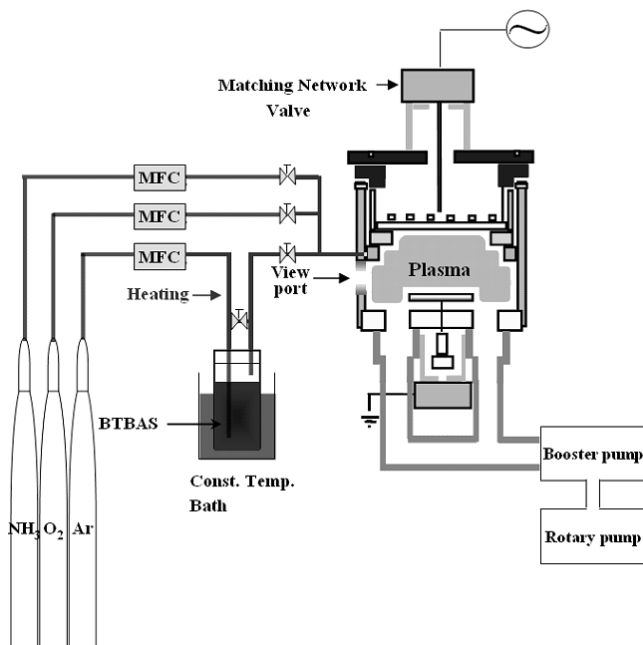


Fig. 1. Schematic diagram of the inductively coupled PECVD apparatus used in this study.

Table 1. Process parameters used for SiO_xN_y film formation

Substrate	Si wafer
Gas chemistry	BTBAS/Ar + O ₂ + NH ₃ O ₂ + NH ₃ = 30 sccm, R = O ₂ /(O ₂ + NH ₃)
Deposition temperature	Low temperature
Source power	300 W
Bias voltage	-80 V
Bubbler temperature	25 °C
Delivery line temperature	80 °C
Flow rate of Ar in BTBAS	8 sccm
Flow rate of O ₂	0 ~ 30 sccm
Flow rate of NH ₃	0 ~ 30 sccm

III. RESULTS AND DISCUSSION

The deposition of SiO_xN_y by PECVD is generally carried out using SiH₄-based gases. However, due to the difficulty in handling the SiH₄ and its explosive nature and the poor step coverage of the films deposited by SiH₄ [5,6], BTBAS was used because it contains nitrogen and is known to form silicon nitride easily at low temperatures when deposited by low-pressure CVD. Figure 2 shows the effect of 30 sccm of O₂/(O₂ + NH₃) on the deposition rate of SiO_xN_y and the refractive index of the deposited SiO_xN_y as measured by ellipsometry. The other process conditions were ICP power of 300 W, a dc bias voltage of -80 V, and a plasma reactor pressure of 80 mTorr at a BTBAS flow rate of 8 sccm in Ar. SiO_xN_y was deposited on a p-type <100>Si substrate at room temperature. As Figure 2 shows, the deposition rate of SiO_xN_y decreased from 113.8 nm/min to 22.8 nm/min with increasing O₂ ratio (defined as O₂/(O₂+NH₃)) from

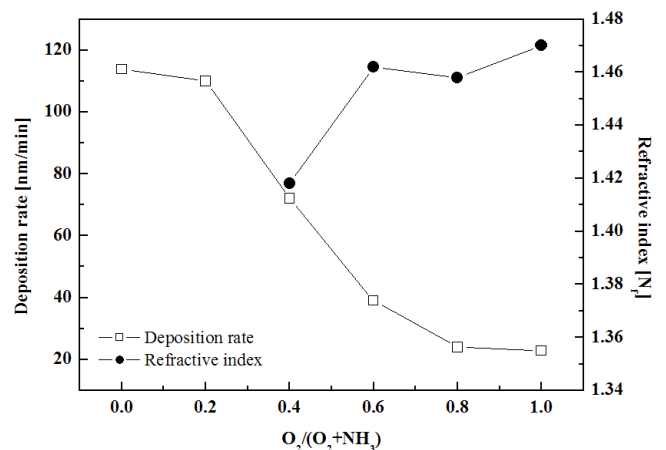


Fig. 2. Deposition rate and refractive index of SiO_xN_y films as functions of the O₂ ratio in feedstock (defined as O₂/(O₂ + NH₃)) fed at a flow rate of 38 sccm (BTBAS/Ar: 8 sccm, (O₂ + NH₃): 30 sccm). A source power of 300 W and a dc bias voltage of -80 V were used.

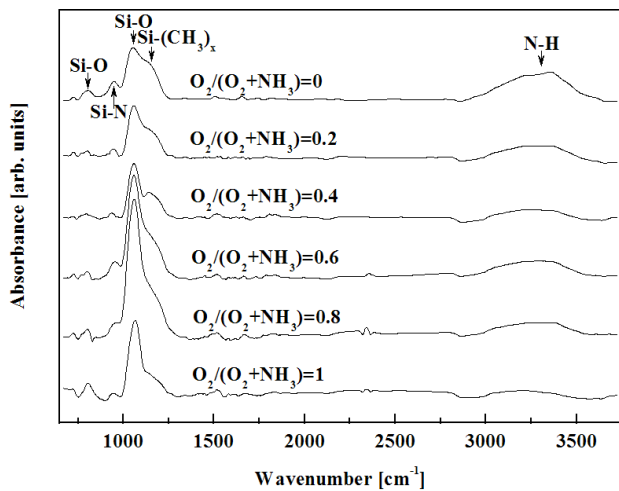


Fig. 3. FT-IR spectra of SiO_xN_y films for various values of the feedstock O₂ ratio. The deposition conditions were the same as those in Figure 3.

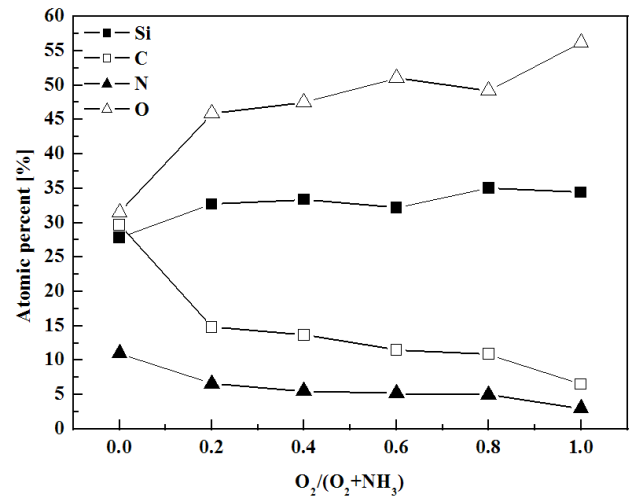


Fig. 4. Atomic percentages in SiO_xN_y films as determined by XPS as a function of the feedstock O₂ ratio. The deposition conditions were the same as those in Figure 3.

0 to 1. When a low oxygen ratio was used, the film was not too soft and was easily scratched during handling. Also, as Figure 2 shows, with increasing oxygen ratio from 0.4 to 1, the index of refraction increased from 1.42 to 1.47; when the oxygen ratio was lower than 0.4, it was difficult to measure the index of refraction. Therefore, we believe that the reduced SiO_xN_y deposition rate and the higher oxygen ratio appear to be related to the removal of -CH from the film and to the formation of a hard SiO_xN_y film. Also, when the oxygen ratio was >0.6, the deposited SiO_xN_y film appeared to have the characteristics of pure SiO₂ and had an index of refraction of 1.46.

Figure 3 shows the FT-IR data of SiO_xN_y films deposited as a function of the oxygen ratio under the same deposition conditions as in Figure 2. This information was obtained to investigate bonding within the deposited films, which were ca. 300-nm thick. As Figure 3 shows, all of the films produced had peaks at 804 cm⁻¹ and 1056 cm⁻¹, which are related to Si-O bonds [10]. In particular, Si-O bonds were observed even without oxygen addition, possibly due to a reaction between the BTBAS and the water vapor in the plasma chamber. A peak corresponding to the Si-N bond was observed near 948 cm⁻¹ in all samples, confirming the formation of SiO_xN_y [12]. However, the peak height of Si-N bond stretching was small, possibly indicating low nitrogen concentrations in the film; moreover, this peak height decreased with increasing oxygen ratio, suggesting a decrease in film Si-N bonds. Even though BTBAS contains nitrogen, the peaks corresponding to Si-N bonds in the deposited SiO_xN_y films were small and became smaller with increasing oxygen ratio, possibly due to the removal of nitrogen with CH from BTBAS by the plasma and by reaction between BTBAS and oxygen. In the deposited films, the peak at 3355 cm⁻¹ corresponding to the N-H

bond and the peak at 1139 cm⁻¹ corresponding to the Si-(CH₃)_x bond also decreased with increasing oxygen ratio [13]. The observed reduction in Si-(CH₃)_x bond absorption in films with increasing oxygen ratio is believed to be related to the removal of CH by oxygen, and the decrease observed in N-H bond absorption is believed to be related to reduced NH₃ levels in the gas mixture. N-H bonds in the film appeared not to depend on NH₃ in the gas mixture on the formation of Si-N bonds in the deposited film by PECVD process. When no oxygen was used (*i.e.*, at an oxygen ratio of 0), due to the significant concentration of N-H bonds (binding energy: 3.5 eV) involved in the deposited film, the films were soft and unstable and showed film staining with time due to the dissociation of NH_x incorporated in film (NH₃ → NH₂ + H, NH₂ → NH + H) [14,15].

Figure 4 shows the composition of the SiO_xN_y films in Figure 3 as a function of O₂/(O₂+NH₃) as measured by XPS. As the figure shows, with increasing oxygen ratio from 0 to 1, the carbon percentage decreased from 29.7 % to 6.5 %, indicating removal of C-H bonds in the film by oxygen. Also, with increasing oxygen ratio, the nitrogen percent was reduced from 11 % to 3 %, the oxygen percentage increased from 31.5 % to 56.2 %, and the silicon percent increased from 27.8 % to 34.4 %. Therefore, XPS produced results similar to the FT-IR data. Also, when the oxygen ratio was >0.6, the composition of the deposited SiO_xN_y films were similar to that of SiO₂. However, the deposited film still showed a low carbon content and the presence of N-H bonds. It is believed that the SiO_xN_y film deposited by high density plasma CVD with biasing using O₂-BTBAS/Ar can be applied as an inorganic transparent film that can be used as a diffusion barrier for polymer materials.

IV. CONCLUSIONS

In this study, a transparent inorganic film of SiO_xN_y was deposited at room temperature (the actual temperature was $<75^\circ\text{C}$ due substrate biasing) by using an inductively coupled plasma CVD and a $\text{NH}_3\text{-O}_2\text{-BTBAS/Ar}$ gaseous feedstock, and the effect of oxygen ratio on the characteristics of the deposited SiO_xN_y films was investigated. When the oxygen ratio was lower than 0.4, the deposited SiO_xN_y film was soft and unstable due to the presence of high C-H and N-H bond densities in the film. With increasing oxygen ratio, the C-H and the N-H bond densities in films decreased. Moreover, the Si-N bond density decreased as the Si-O bond density increased. Therefore, when oxygen ratios were >0.6 , oxygen-rich SiO_xN_y resembling SiO_2 with a refractive index of 1.46 was obtained. The oxygen-rich SiO_xN_y films obtained using $\text{O}_2\text{-BTBAS/Ar}$ feedstock were stable, hard, and transparent, and thus are applicable as inorganic transparent diffusion barriers for polymer materials.

ACKNOWLEDGMENTS

This work was supported by the Ministry of Commerce, Industry and Energy, and by the National Research Laboratory Program (NRL) of the Korean Ministry of Science and Technology. We thank Mecharonics (Mecharonics, Inc.) for donating the BTBAS.

REFERENCES

- [1] S. Arulkumaran, T. Egawa, H. Ishikawa, T. Jimbo and Y. Sano, *Appl. Phys. Lett.* **84**, 613 (2004).
- [2] Heiko Stegmann, Ehrenfried Zschech, *Appl. Phys. Lett.* **83**, 5017 (2003).
- [3] F. J. H. van Assche, R. T. Vangheluwe, J. W. C. Maes, W. S. Mischke, M. D. Bijker, F. C. Dings and M. F. J. Evers, *SID'04 DIGEST* 695, (2004).
- [4] Shashank C. Deshmukh and Eray S. Aydil, *Appl. Phys. Lett.* **65**, 3185 (1994).
- [5] C. S. Pai and C. P. Chang, *J. Appl. Phys.* **68**, 793 (1990).
- [6] J. Y. Lee and S. H. Lee, *J. Korean Phys. Soc.* **45**, 558 (2004).
- [7] R. K. Laxman, T. D. Anderson and J. A. Mestemacher, *Solid State Technol.* **43**, (2000).
- [8] J. Irvén, *J. Mater. Chem.* **14**, 3071 (2004).
- [9] B. J. Park, R. Conti, L. Economikos and A. Chakravarti, *J. Vac. Sci. Technol. B* **19**, 1788, (2001).
- [10] J. S. Jong, J. Y. Kwon, Y. S. Park, D. Y. Kim, H. S. Cho, K. B. Park, W. Xianyu, H. Kim and T. Noguchi, *J. Korean Phys. Soc.* **45**, S861 (2004).
- [11] J. H. Lee, C. H. Jeong, J. T. Lim, N. G. Jo, S. J. Kyung and G. Y. Yeom, *J. Korean Phys. Soc.* **46**, 890 (2005).
- [12] H. Ono, T. Ikarashi and Y. Miura, *Appl. Phys. Lett.* **74**, 203 (1999).
- [13] R. Gonzalez-Luna, M. T. Rodrigo, C. Jimenez and J. M. Martinez-Duart, *Thin Solid Films* **317**, 347 (1998).
- [14] H. Caquineau and B. Despas, *Chem. Eng. Sci.* **52**, 2901 (1997).
- [15] S. H. Bae, D. G. Farber and S. J. Fonash, *Solid-State Electronics* **44**, 1355 (2000).