

# Electrical and Optical Properties of Nitrogen-Incorporated Silicon-Oxide Films by Using Plasma-Enhanced Chemical-Vapor Deposition with Tetramethoxysilane /N<sub>2</sub>O/NH<sub>3</sub> Gas

C. J. CHUNG, T. H. CHUNG,\* M. S. KANG and Y. KIM  
*Department of Physics, Dong-A University, Busan 604-714*

(Received 24 August 2005)

Nitrogen-incorporated silicon-oxide thin films have been deposited by using inductively coupled plasma-enhanced chemical-vapor deposition with tetramethoxysilane (TMOS), N<sub>2</sub>O, and NH<sub>3</sub> gas mixtures. The chemical bonding states and compositions of the deposited films are analyzed by Fourier transform infrared (FTIR) spectroscopy and by X-ray photoelectron spectroscopy, and in-situ ellipsometry measurements are performed on the deposited films for optical characterization. The effects of the partial pressure ratio of TMOS to N<sub>2</sub>O and the radio-frequency input power on the properties of the film are investigated. Capacitance-voltage measurements are performed in metal-oxide-semiconductor capacitors to obtain the electrical properties of the deposited films. As the partial pressure of N<sub>2</sub>O decreases, the refractive index begins to decrease, reaches a minimum, and then increases again. We attribute the variation of the refractive index to the incorporation of oxygen, carbon, and nitrogen atoms. FTIR absorption bands are observed from about 850 to 1000 cm<sup>-1</sup> and 1120 to 1180 cm<sup>-1</sup>, and can be attributed to the formation of a nitrogen-incorporated silicon-oxide film. The fixed charge density increases first, has a maximum, and decreases with increasing N<sub>2</sub>O fraction while the interface trap density increases with increasing N<sub>2</sub>O fraction.

PACS numbers: 52.75Rx, 52.25-b, 73.90+f

Keywords: Silicon-oxynitride film, PECVD, Organosilicon source

## I. INTRODUCTION

Nitrogen-incorporated silicon-oxide thin films are being widely used as thin gate dielectrics and passivation layers in microelectronic circuits because they have a higher dielectric constant and more effective barrier property for boron diffusion than silicon-oxide thin films [1]. They have also been used as optical waveguides for micromechanical systems because of their excellent properties, such as their continuously varying refractive index with changing oxygen and nitrogen content inside the material [2, 3]. For this reason, a good knowledge of their characteristics, such as composition, refractive index, and electrical properties is needed.

Nitrogen-incorporated silicon-oxide thin films can be formed either by high-temperature or low-temperature techniques. Plasma-enhanced chemical-vapor deposition (PECVD), remote PECVD, and low-pressure CVD are typical low-temperature processes while rapid thermal processes and nitridation of SiO<sub>2</sub> films in NH<sub>3</sub> or N<sub>2</sub> atmospheres are typical high-temperature processes [1]. The merits of a PECVD process, such as the film quality,

the deposition rate, and the deposition uniformity, are closely connected to the species transport and reactions in plasma as well as the reactions on the wafer surfaces [4].

Up to now, the deposition of silicon-oxynitride films by PECVD has mainly utilized silane (SiH<sub>4</sub>) and nitrous oxide (N<sub>2</sub>O) [1, 5, 6] or a mixture of SiCl<sub>2</sub>H<sub>2</sub> - NH<sub>3</sub> - N<sub>2</sub>O [7]. PECVD of silicon dioxide from organosilicon sources and oxygen gas has been extensively investigated and has proven to provide good-quality conformal films [4, 8–11]. In this study, nitrogen-incorporated silicon-oxide thin films are prepared in a PECVD reactor using a mixture of TMOS (tetramethoxysilane: Si(OCH<sub>3</sub>)<sub>4</sub>), N<sub>2</sub>O, and NH<sub>3</sub> as precursor gases. The film's optical properties are characterized by refractive index measurements using in-situ ellipsometry. The characterization of the film's layers is also performed by using ex-situ Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). Specifically, the aim of this paper is to study the effects of the partial pressure ratio of TMOS and N<sub>2</sub>O in the gas, for a fixed partial pressure of NH<sub>3</sub> of 5 % and fixed RF input power, on the electrical and the optical properties of the deposited film. The variation of the refractive index is discussed

\*E-mail: thchung@dau.ac.kr; Fax: +82-51-200-7232

in relationship with the deposition rates and the FTIR spectra.

## II. EXPERIMENT

The PECVD reactor utilizes an inductively coupled plasma source operating at 13.56 MHz to sustain low-pressure (1 – 50 mTorr) high-density plasmas. The inductively coupled plasma yields a high degree of ionization and significant decomposition of the precursor. The gas flows of TMOS, N<sub>2</sub>O and NH<sub>3</sub>, regulated by mass flow controllers (AFC 50), are introduced downstream from the plasma about 10 cm above the substrate. The films are deposited on p-type Si (100) substrates at room temperature.

The plasma chamber consists of a stainless-steel cylinder with a 28-cm diameter and a 34-cm length. A 1.9-cm-thick by 27-cm-diam tempered glass plate mounted on one end separates the planar one-turn induction coil from the plasma. The induction coil is made of copper (with water-cooling) and is connected to an L-type capacitive matching network and the radio-frequency (rf) power generator (ENI OEM-12). To control the ion bombardment energy, the electrode on which the substrate is placed can be independently driven by a capacitively coupled rf source. Hence, independent control of the ion/radical flux (through the ICP power) and the ion bombardment energy (through the substrate bias power) is possible.

The partial pressures of the organosilicon compound, and N<sub>2</sub>O, and NH<sub>3</sub>, are controlled with mass flow controllers. The total pressure is fixed at 10 mTorr. The ICP power is varied from 300 W to 1000 W, and a substrate bias power is not applied. For a fixed partial pressure of NH<sub>3</sub> of 5 %, the parameter *R* is defined as the ratio of partial pressure of the TMOS gas to that of the N<sub>2</sub>O gas (*i.e.*  $R = p(\text{TMOS}) / p(\text{N}_2\text{O})$ ). Deposition studies are carried out as functions of the radio-frequency input power and the N<sub>2</sub>O fraction (*R*). The samples are numbered from N1 [ $(p(\text{N}_2\text{O}) + p(\text{NH}_3)) : p(\text{TMOS}) = 1 : 9$ ] to N9 [ $(p(\text{N}_2\text{O}) + p(\text{NH}_3)) : p(\text{TMOS}) = 9 : 1$ ]. Ellipsometry measurements using the in-situ ellipsometer (Elli-situ 2000, Ellipso Tech) operating at the He-Ne laser wavelength (632.8 nm) are performed to obtain the thickness and the refractive index of the films. Both the incidence and the outlet angles are 70 degree. The deposition rate is determined from the ratio of the film thickness to the deposition time. The chemical bonding states and the composition of the deposited films are analyzed by using FTIR (BIO RAD Excalibur) and XPS (ESCA/Auger System). High-frequency capacitance-voltage (C-V) measurements are performed using a probe connected to a computer-controlled capacitance-meter (Keithley 590). The C-V samples are prepared in a way such that thermally evaporated Al is used as the Si back electrode and as the capacitor electrode.

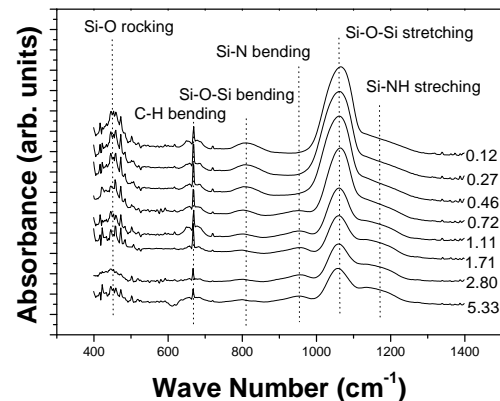


Fig. 1. FTIR spectra for films deposited at various partial pressure ratios, where  $P = 500$  W and  $p = 10$  mTorr.

## III. RESULTS AND DISCUSSION

Fig. 1 shows FTIR spectra of films deposited at various values of the partial pressure ratio. The ICP power is fixed at 500 W. The spectra are obtained from films with the same thickness (200 nm). The TMOS, N<sub>2</sub>O, and NH<sub>3</sub> can be dissociated by the plasma, and radicals such as Si, O, C, N, and CH form the film on the substrate [12]. The spectra exhibit absorption peaks at 1045 – 1075 cm<sup>-1</sup> corresponding to the Si-O-Si stretching band, at 810 cm<sup>-1</sup> corresponding to the Si-O-Si bending mode, and at 460 cm<sup>-1</sup> corresponding to the Si-O-Si rocking mode [9, 13, 14]. The peak around 670 cm<sup>-1</sup>, which was not present in the TMOS/N<sub>2</sub>O case, is related to the bending vibrations of SiCH<sub>3</sub>. The peak around 960 cm<sup>-1</sup> is most probably related to the stretching vibrational mode of Si-N-Si bonds, which is evidence that nitrogen incorporates in the oxide network [15, 16]. Since the nitrogen content in the film is only few percent, the Si-N peak at 960 cm<sup>-1</sup> appears as a shoulder on a strong Si-O-Si stretching mode. In addition, there are weak and shallow bands that appear within 1120 – 1180 cm<sup>-1</sup>, which are attributed to the bending vibration of the NH bonds in the oxynitride network. The strongest peak in the infrared spectrum of the film appears at 1070 cm<sup>-1</sup>, and it shifts toward lower wavelength with increasing *R* [1, 17, 18]. A similar trend was observed for silicon-oxynitride films deposited by using PECVD with a SiH<sub>4</sub>/N<sub>2</sub>O gas mixture [19]. As *R* increases, the films become less absorbent, and the full width at half maximum of the peak increases. The absorption bands around 960 cm<sup>-1</sup> and at 1120 – 1180 cm<sup>-1</sup>, which can be attributed to the formation of a nitrogen-incorporated oxide, become dominant as *R* increases. As the partial pressures of N<sub>2</sub>O, and NH<sub>3</sub> decrease (*R* increases), nitrogen incorporation in the films is evident (N2-N5). Although more of the carbon species is in the feed in the form of more TMOS, less CH bond is observed in the FTIR spectra,

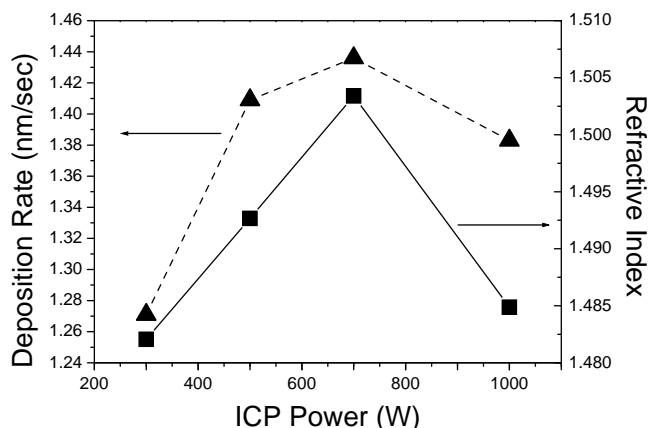


Fig. 2. Deposition rate and index of refraction as functions of the ICP power, where  $R = 5.3$  and  $p = 10$  mTorr.

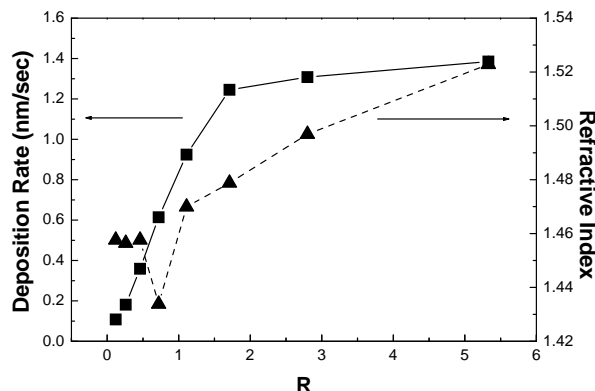


Fig. 3. Deposition rate and index of refraction as functions of the partial pressure ratio of TMOS and  $N_2O$ ,  $R$ , where  $P = 500$  W and  $p = 10$  mTorr.

which seems to contribute to the increase in the refractive index [20]. A similar behavior to this was observed in the cases of methoxy-group organosilicon compounds [9].

In Fig. 2, the deposition rate is found to increase with increasing ICP power from 300 W to 700 W and to decrease slightly at 1000 W. The refractive index shows a similar variation to that of the deposition rate. Generally, an increase in the incident power leads to an enhancement of the electron energy and, thus, to a higher fragmentation of the monomer in the gas phase. In the present case, however, at low power,  $N_2O$  gas is decomposed into O and  $N_2$ . As the power increases, the reactions  $N_2O + O \rightarrow 2 NO$  and  $NO + O \rightarrow NO_2$  are expedited. This is the reason the nitrogen composition decreases with a further increase in the input power, and the refractive index, which is proportional to the nitrogen content in the film, has a maximum at  $P = 700$  W. Since the ICP power provides an effective activation en-

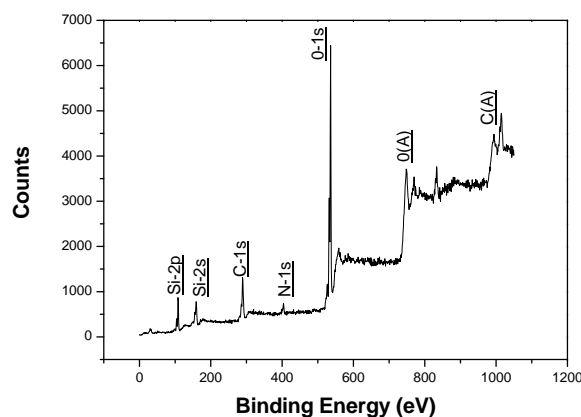


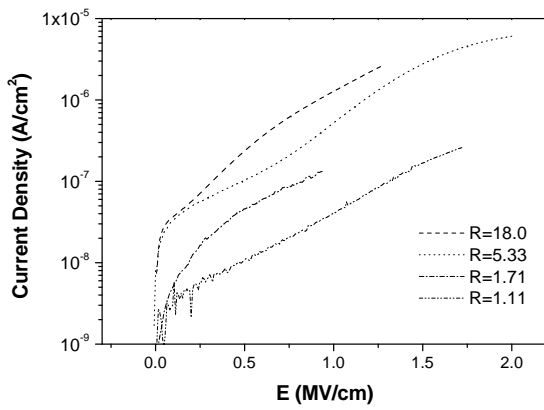
Fig. 4. Typical XPS spectrum of the nitrogen-incorporated silicon oxide thin film obtained from TMOS/  $N_2O/NH_3$ .

ergy for ionization and heating of gas, an increase in the ICP power results in an increase in the deposition rate, but for a further increase in the ICP power results in high ion-flux, which promotes etching of the deposited films. Therefore, the deposition rate decreases again with increasing ICP power.

Fig. 3 shows the deposition rate and the refractive index as functions of  $R$ . The ICP power and the total pressure are kept constant at 500 W and 10 mTorr, respectively. An increase in the TMOS partial pressure is observed to cause an increase in the deposition rate. A similar trend is found in the case of HMDSO/ $O_2$  where the deposition rate depends linearly on the HMDSO concentration [21]. As we can see, the refractive index lies between 1.43 and 1.53. These values are little higher than that of thermal  $SiO_2$  ( $n = 1.456$ ). However, these values are quite low compared to those of  $SiON$  (between 1.6 and 1.9) [7]. As  $R$  increases, the refractive index decreases first, reaches a minimum at  $R = 0.72$ , and then increases again. In a previous work [11], we found the refractive index of silicon-oxide films deposited from organosilicon sources, such as TMOS/ $O_2$ , to be a little lower than that of thermally grown silicon oxides. We attribute the decrease in the refractive index to the incorporation of more oxygen. Also, the abundances of nitrogen and carbon in the films contribute to the increase in the refractive index. Around  $R = 0.72$ , the oxygen content in the gas phase reaches a high level because  $N_2O$  and TMOS produce O atoms, and the carbon and the nitrogen contents in the films begin to increase (see Table 1), therefore, the refractive index reaches a minimum. In a previous paper working on the TMOS/ $N_2O$  case [22], we observed that the oxygen content in the gas phase of a TMOS/ $N_2O$  discharge and in the deposited films is maximal at  $R = 0.66$ . We also observed by using optical emission spectroscopy and XPS that the oxygen content in the gas phase showed a similar trend to the oxygen content in the deposited films. Although the role

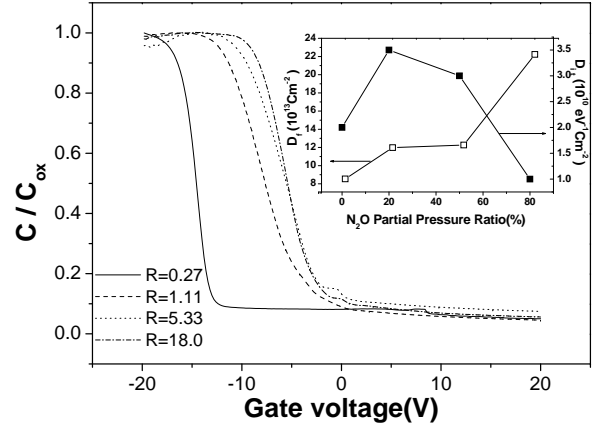
Table 1. Film composition as measured by XPS.

Sample	$R = (P_{TMOS}/P_{N_2O})$	Composition(at.%)			
		Si	O	C	N
N9	0.12	32.1	61.8	6.1	0
N8	0.27	31.9	60.1	8	0
N7	0.46	30.3	61.9	6.7	1.1
N6	0.72	29.2	56.8	12.6	1.3
N5	1.11	22.7	53.9	20.6	2.8
N4	1.71	20.9	49.3	25.8	4.1
N3	2.80	19	46.8	29.8	4.4
N2	5.33	19.8	45.2	31.6	3.4

Fig. 5. I-V curves of the films deposited at different partial pressure ratios, where  $P = 500$  W and  $p = 10$  mTorr.

of the oxygen atoms is assumed to be dissociation of TMOS molecules, they are also responsible for the elimination of C and H atoms from the growing films [23]. For a lower oxygen fraction in the gas, the refractive index increases due to the incorporation of the carbon species [24,25]. We may attribute the increase in the refractive index to the incorporation of more nitrogen and more carbon. It was previously shown in different PECVD reactors utilizing organosilicon sources that the refractive index decreased with increasing oxygen concentration at a fixed flow rate of precursor molecules [10,26,27].

Above predictions are confirmed with X-ray photoelectron spectroscopy. A typical XPS spectrum is shown in Fig. 4. The films exhibit a weak N 1s peak, but its intensity is at the limit of noise, precluding a quantitative analysis of the nitrogen content in the films. The evolution of the composition of the films expressed as percentage of atoms obtained from XPS measurement is shown in Table 1. The results show that the nitrogen content in the films increases with  $R$ . This result is in agreement with the discussion of the refractive index measurement in Fig. 3. The films prepared from TMOS contain carbon impurities. The carbon content increases with the partial pressure of TMOS. The increase in the refractive index with increasing  $R$  can be explained by a larger in-

Fig. 6. C-V curves of the films deposited at different  $N_2O$  partial pressure ratios, where  $P = 500$  W and  $p = 10$  mTorr. The inset shows the variations of the interface trap density ( $D_{it}$ ) and fixed oxide charge density ( $D_f$ ) with the  $N_2O$  partial pressure ratio.

corporation of the carbon species. The Si 2p, O 1s, and C 1s peaks are located at binding energies of 108.5 eV, 536.1 eV, and 289.7 eV, respectively. The reported peak positions for silicon oxide obtained from TMOS/ $O_2$  were 103.65 eV, 532.34 eV, and 284.78 eV, respectively [28]. The N 1s peak position is 403.6 eV. This suggests that the bond structure is  $Si_2 = N-O-Si$  [29].

The current-voltage (I-V) characteristics measured at room temperature are shown in Fig. 5. The N1 sample ( $R = 18.0$ ) has the highest current density through the dielectrics. Although the breakdown field is lower than that of a thermal oxide, the leakage current is comparable to that of the thermal oxide due to an improvement of the interface state [30]. The specific resistivity of the dielectric film is evaluated from the linear part of the I-V curves. The N1 sample has a slightly larger specific resistivity.

Fig. 6 shows the C-V curves of the silicon-oxynitride films deposited at different  $R$ . The C-V curves are shifted to negative voltage. A negative flat-band voltage ( $V_{fb}$ ) indicates the presence of positive charges in the oxynitride films. These positive charges are defects, which are usually holes trapped at oxygen vacancies [31]. The  $V_{fb}$  becomes more negative with increasing  $N_2O$  fraction in the gas because an increasing  $N_2O$  fraction increases the number of oxygen-vacancy defects. The interface trap density  $D_{it}$  and the fixed charge density  $D_f$  are calculated by fitting the C-V curves with a theoretical curve. The theoretical curve is obtained by a numerical integration of the semiconductor depletion capacitance presented in Ref. 32. The model assumes constant  $D_{it}$  through the Si energy gap, and this assumption is sufficient for the scope of the present study. As the inset of Fig. 5 shows,  $D_f$  increases with increasing  $N_2O$  fraction. The high fixed charge densities can be reduced significantly by using a rapid thermal annealing process [1].

The interface trap density increases first, has a maximum, and decreases with increasing  $N_2O$  fraction. The trend is expected because the nitrogen content in the films is maximal for the  $N_2$  sample ( $R = 2.80$ ), which can be seen from the FTIR spectra and from the refractive-index variation. The level of  $D_{it}$  is lower than that obtained for films deposited from a  $SiH_4/N_2O$  precursor [1], which can be attributed to less nitrogen atoms being incorporated at the Si-SiON interfaces than in the  $SiH_4/N_2O$  case. Excess oxygen or impurities (carbon or NH) might also act as trap sites in the films [33]. The general tendency presented here is in agreement with the  $SiH_4/N_2O$  case [1] and the  $O_2/(HMDS+He)$  case [8], but in contrast to the TEOS/ $O_2$  case [28] and the TMOS/ $O_2$  case [34].

#### IV. CONCLUSION

Plasma-enhanced chemical-vapor deposition of nitrogen-incorporated silicon-oxide thin films using tetramethoxysilane,  $N_2O$ , and  $NH_3$  gas was performed in an inductively coupled RF discharge. A FTIR absorption band from about 850 to 1000  $cm^{-1}$ , which could be attributed to the formation of silicon oxynitride was observed. The optical characteristics of the deposited films were studied by varying the TMOS to  $N_2O$  pressure ratio. As the partial pressure of  $N_2O$  was decreased, the refractive index began to decrease, reached a minimum at  $R = 0.72$ , and then increased again. We attribute the decrease in the refractive index to the incorporation of more oxygen. Also, the abundances of nitrogen and carbon in the films contributed to the increase in the refractive index. The fixed charge density increased with increasing  $N_2O$  fraction while the interface trap density increased first, had a maximum, and decreased with increasing  $N_2O$  fraction. Future work will find gas mixtures that maximize the nitride deposition rates and reduce the oxide deposition rates. For this purpose, a gas mixture of tetramethylsilane/ $N_2/NH_3$  is being considered.

#### ACKNOWLEDGMENTS

This work is supported by a research grant of Dong-A University (program year of 2004).

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