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Plasma enhanced chemical vapor deposition of nitrogen-incorporated silicon oxide films using TMOS/N_2O gas

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Abstract

Plasma enhanced chemical vapor deposition (PECVD) of nitrogen-incorporated silicon oxide thin films using TMOS (tetramethoxysilane) and N_2O plasma is studied. The effects of the TMOS and N_2O pressure ratio on the properties of the film and the plasma are investigated. The intensities of light emission from molecules and radicals in the plasma are measured by optical emission spectroscopy (OES). The deposited films are analyzed by in-situ ellipsometry, and Fourier transform infrared spectroscopy (FTIR). The optical properties are measured by photoluminescence (PL). As the partial pressure of N_2O decreases, the refractive index begins to decrease, reaches a minimum, and then increases again. When the oxygen content in the plasma phase reaches a maximum, the refractive index reaches a minimum. We attribute the decrease of the refractive index to the incorporation of more oxygen. The FTIR absorption band from about 850 to 1000 cm^{-1}, which can be attributed to the formation of SiON is observed. A broad PL appears around 1.9–2.4 eV. As the oxygen content increases, the PL spectrum shifts toward a higher energy.
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Keywords: Nitrogen-incorporated silicon oxide film; PECVD; Organosilicon source

1. Introduction

Nitrogen-incorporated silicon oxide thin films are being widely used not only as masking and passivation layers in microelectronic circuits but also in optical filter fabrication because of their excellent properties such as continuously variable refractive index [1,2]. For this reason, a good knowledge of their characteristics (layer structure, thickness, composition and refractive index) is needed. In this study, nitrogen-incorporated silicon oxide thin films are prepared with the purpose of optical applications in a PECVD reactor using TMOS (tetramethoxysilane: $Si(OCH_3)_4$) and N_2O as precursor gases.

In PECVD, the plasma is used as an aid to chemically decompose the vapor precursor and as a source of active species involved in the film growth. The energy of deposition is controlled by the electric field at the surface of the growing film. It has been suggested that low-temperature deposition by PECVD can become practical when combined with ion bombardment during the film growth by applying an electrical bias to the substrate [4]. The merits of a PECVD process such as the film quality, deposition rate, and deposition uniformity are closely connected to the species transport and reactions in plasma as well as the reactions on the wafer surfaces [3].

The plasma is characterized using optical emission spectroscopy. The correlation between the film properties and the plasma characteristics is explained to some extent. The film's optical properties are characterized by the refractive index measurements using in-situ ellipsomety. The characterization of the SiO_2 layers are also performed by ex-situ Fourier transform infrared spectroscopy (FTIR). Specifically, the aim of this paper is to study the effects of the TMOS and N_2O pressure ratio in the gas on the optical properties of the deposited film. The variation of the refractive index is discussed in relationship with the deposition rates, the FTIR spectra, OES spectra, and PL spectra.

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2. 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. Oxygen gas flow and TMOS, regulated by mass flow controllers (AFC 50), are introduced downstream from the plasma about 10 cm above the substrate. Films are deposited on p-type Si (100) substrate at room temperature.

The plasma chamber consists of a stainless-steel cylinder with 28 cm diameter and 34 cm length. A 1.9-cm-thick by 27-cm-diameter tempered glass plate mounted on one end

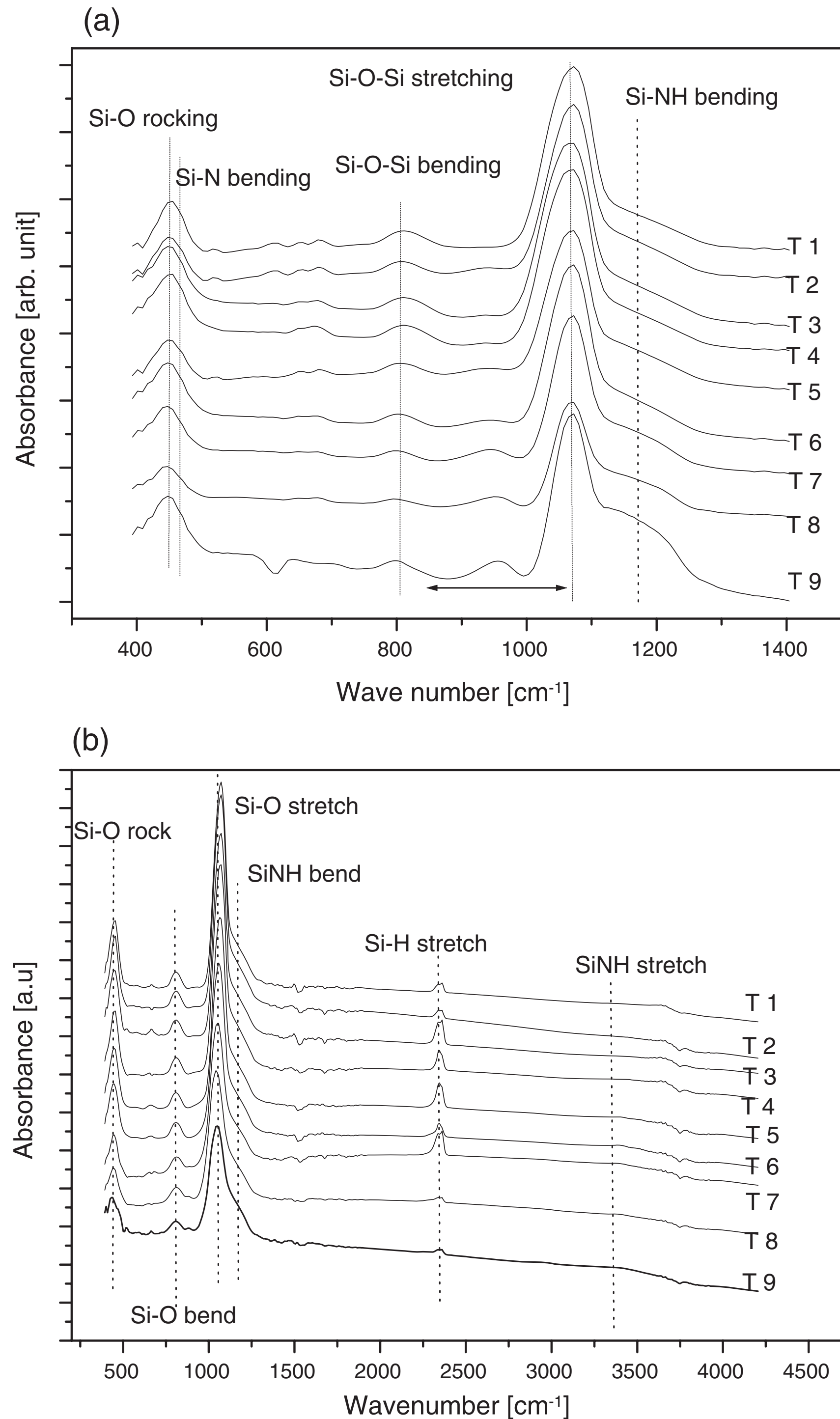

Fig. 1. (a) FTIR spectra for films deposited at various TMOS and N_2O pressure ratio, R, where P = 500 W, p_{total} = 10 mTorr. (b) FTIR spectra where P = 300 W, p_{total} = 10 mTorr.

separates the planar one-turn induction coil from the plasma. The induction coil is made of copper (with water-cooling) and connected to an L-type capacitive matching network and an 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 pressure of the organosilicon compound and that of oxygen gas were controlled by mass flow controllers. The total pressure is fixed at 10 mTorr. The parameter R is defined as the ratio of partial pressure of the TMOS gas to the N_2O gas (i.e. $R = p_{TMOS}/p_{N_2O}$). Deposition studies were carried out as functions of the radio frequency power and N_2O fraction (R). The samples are numbered from T1 ($p_{TMOS}/p_{N_2O} = 1{:}9$) to T9 ($p_{TMOS}/p_{N_2}O = 9{:}1$). The thickness and refractive index was measured using the in-situ ellipsometer (Elli-situ 2000, Ellipso Tech). The deposition rate was determined from the ratio of the film thickness to the deposition time. The chemical bonding states of deposited films were analyzed by FTIR (BIO RAD Excalibur).

The light intensities of emissive molecules and radicals in the plasma was collected by an optical fiber that was coupled to multi-channel spectrometer (OPC-2000). Emission light from glow discharge is detected through a homemade optical probe during deposition in the wavelength range of 250–700 nm with a resolution of 1 nm. The dependence of the emission intensities on process parameters is investigated.

Photoluminescence were excited by 488 nm Ar^+ ion laser (30 mW and ~1 mm beam diameter) mechanically chopped at a frequency of 500 Hz. PLs were dispersed by a 0.5 m monochromator and detected by a photomultiplier tube (Hamamatsu R928) by using standard lock-in technique.

3. Results and discussion

Fig. 1(a) shows FTIR spectra of films deposited at various values of R. The ICP power is fixed at 500 W. The spectra were obtained from films with the same thickness (200 nm). The spectra exhibit absorption peaks corresponding to Si–O–Si stretching band at 1045–1075 cm^{-1}, Si–O–Si bending at 810 cm^{-1}, Si–O–Si rocking mode at 460 cm^{-1} [4–6]. The absorption band (850–1000 cm^{-1}), which can be attributed to the formation of nitrogen-incorporated oxide, becomes dominant as the R increases (T8, T9). As the nitrogen content increases, the absorption bands were broadened and shifted to lower wave numbers (T8, T9) [7,8]. In addition there are also SiNH bending mode and silicon atom breathing modes evident at 1175 cm^{-1} and 475 cm^{-1}, respectively. Fig. 1(b) is the FTIR spectra taken at $P = 300$ W. The spectra exhibits absorption peaks corresponding to Si–O–Si stretching at 1062 cm^{-1}, Si–O–Si deformation at 796 cm^{-1}, Si–O–Si stretching at 440 cm^{-1}. The absorption at 2250 cm^{-1} is assigned to Si–H stretching vibrations [9]. For samples T8 and T9, this band is very weak. The absorption peak is maximum at $R = 1$. The results indicate that the number of Si–H bonds increases when the nitrogen content in the deposits is low.

Fig. 2 shows the deposition rate and refractive index. The dependence of the deposition rate on TMOS/N_2O pressure ratio is shown. The ICP power and the total pressure are kept constant at 500 W and 10 mTorr, respectively. No substrate bias power is applied. Starting from N_2O only case, the deposition rate increases with an addition of TMOS. A similar trend is found in the case of HMDSO/O_2

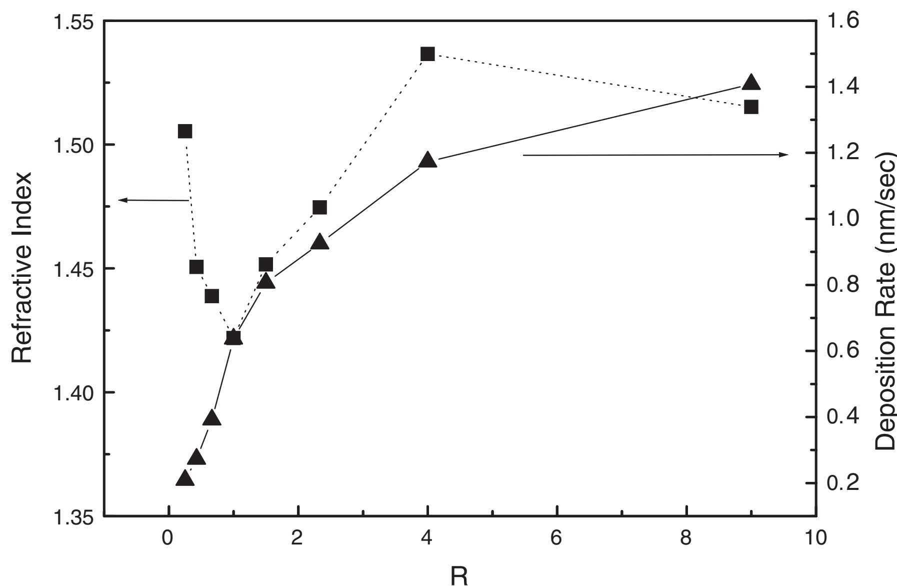

Fig. 2. Deposition rate and index of refraction as a function of TMOS and N_2O pressure ratio, R, where $P = 500$ W, $p_{total} = 10$ mTorr.

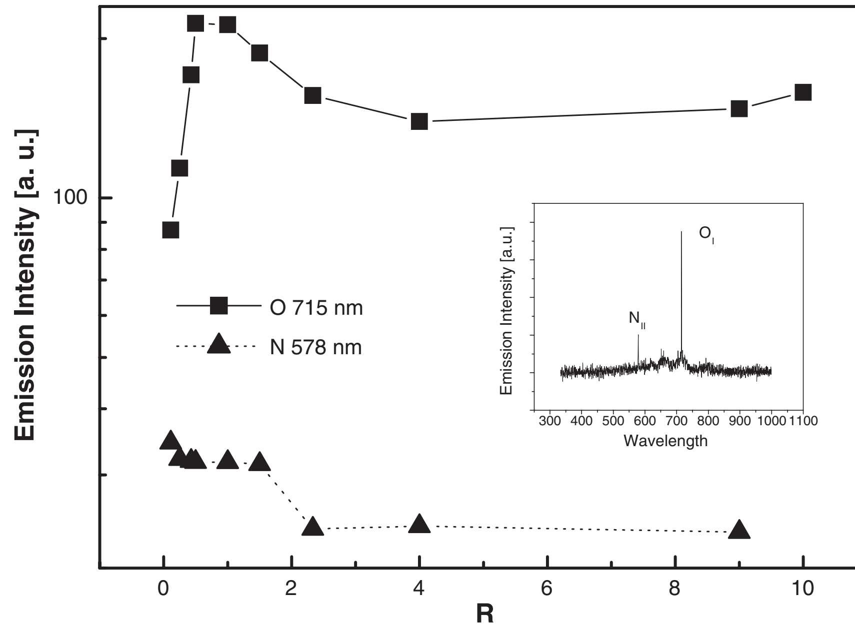

Fig. 3. Optical emission spectrum of TMOS and N_2O plasma for various TMOS and N_2O pressure ratio where $P = 500$ W, $p_{total} = 10$ mTorr.

where the deposition rate depends linearly on the HMDSO concentration [10]. As can be seen, the refractive index lies between 1.43 and 1.53. These values are a little higher than that of thermal SiO_2 ($n \simeq 1.456$). However, these values are quite low compared to those of other SiON (between 1.6 and 1.9) [11]. As the R increases, the refractive index decreases, reaches a minimum at $R = 1$, and than increases again. We attribute the decrease of the refractive index to the incorporation of oxygen. Around $R = 1$, the oxygen content reaches maximum since N_2O and TMOS produce O atom, therefore the refractive index reaches a minimum. Although the role of oxygen atoms is assumed to dissociate TMOS molecules, they are also responsible for the elimination of C and H atoms from the growing films [12]. For lower oxygen fraction in the gas, the refractive index increases due to incorporation of carbon species [13,14]. We can attribute the decrease of the refractive index to the incorporation of more oxygen. 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 [15–17]. For $R < 0.25$, $R > 4$ the refractive index has higher values.

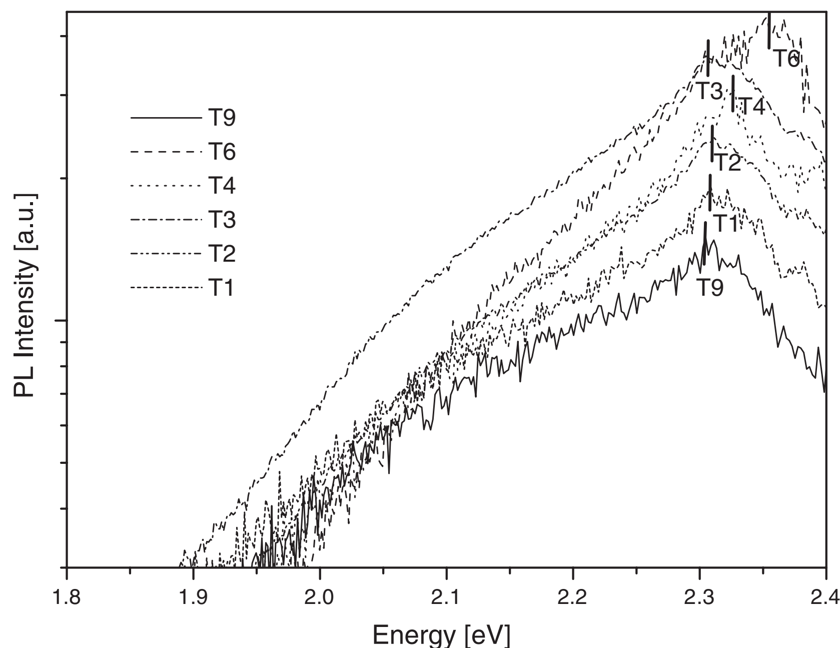

Fig. 4. Photoluminescence spectra for various TMOS and N_2O pressure ratio where $P = 500$ W, $p_{total} = 10$ mTorr.

Optical emission spectroscopy measurements revealed the strong emission features of O_I (715.6 nm), N_{II} (578.8 nm). Besides, there are peaks of N_{II} (660 nm), N_V (671.8 nm), N_V (685–688 nm). Fig. 3 shows the evolution of emission intensity peaks of O_I (715.6 nm) and N_{II} (578.8 nm) from oxygen and nitrogen atom as a function of TMOS/N_2O pressure ratio. Around $R=1$, the oxygen content reaches maximum. Future work is to find gas mixtures that maximize the nitride deposition rates, reduce the oxide deposition rates, and minimize the hydrogen incorporation.

It has been known that photoluminescence from silicon oxynitride or silicon nitride results from Si–N bonds [18]. These films contain many defects and localized states, especially when they are prepared by plasma enhanced chemical vapor deposition. Fig. 4 shows typical PL spectra observed at room temperature. A Gaussian-shaped broad PL appears around 1.9–2.4 eV. As the oxygen content increases, the PL spectrum shifts toward a higher energy (T4, T6) where the refractive index of the deposited film has small values. These characteristics are in agreement with other experiments [18].

4. Conclusion

Plasma enhanced chemical vapor deposition of nitrogen-incorporated silicon dioxide thin films using tetramethoxysilane and N_2O gas was investigated in an inductively coupled RF discharge. The FTIR absorption band from about 850 to 1000 cm^{-1}, which can be attributed to the formation of silicon oxynitride, are observed. The optical characteristics of the deposited films have been studied with varying TMOS and N_2O pressure ratio. As the partial pressure of N_2O decreases, the refractive index begins to decrease, reaches a minimum at $R=1$, and than increases again. When the oxygen content in the plasma phase reaches a maximum, the refractive index reaches a minimum. We attribute the decrease of the refractive index to the incorporation of more oxygen. A broad PL appears around 1.9–2.4 eV. As the oxygen content increases, the PL spectrum shifts toward a higher energy.

Acknowledgments

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References

[1] K.E. Mattsson, J. Appl. Phys. 77 (1995) 6616.
[2] M.N.P. Carreno, M.I. Alayo, I. Pereyra, A.T. Lopes, Sens. Actuators, A 100 (2002) 295.
[3] S.C. Deshmukh, E.S. Aydil, J. Vac. Sci. Technol., A 13 (1995) 2355.
[4] Y. Inoue, H. Sugimura, O. Takai, Thin Solid Films 345 (1999) 90.
[5] A.D. Nara, H. Itoh, Jpn. J. Appl. Phys. 36 (1997) 1477.
[6] D.V. Tsu, G. Lucovsky, M.J. Mantini, J. Vac. Sci. Technol., A 5 (1987) 1999.
[7] L. Torrison, J. Tolle, J. Kouvetakis, S.K. Dey, D. Gu, J. Non-Cryst. Solids 288 (2001) 88.
[8] J. Viard, E. Beche, D. Perernau, R. Berjoan, J. Durand, J. Eur. Ceram. Soc. 17 (1997) 2025.
[9] K. Teshima, Y. Inoue, H. Sugimura, O. Takai, Surf. Coat. Technol. 146–147 (2001) 451.
[10] J.A. Theil, J.G. Brace, R.W. Knoll, J. Vac. Sci. Technol., A 12 (1994) 1365.
[11] M. Modreanu, M. Gartner, N. Tomozeiu, J. Seekamp, P. Cosmin, Opt. Mater. 17 (2001) 145.
[12] C. Vallee, A. Granier, K. Aumaille, C. Cardinaud, A. Goullet, N. Coulon, G. Turban, Appl. Surf. Sci., A 138–139 (1999) 57.
[13] C. Vallee, A. Goullet, F. Nicolazo, A. Granier, G. Turban, J. Non-Cryst. Solids 216 (1997) 48.
[14] A. Goullet, C. Vallee, A. Granier, G. Turban, J. Vac. Sci. Technol., A 18 (2000) 2452.
[15] A. Grill, V. Patel, J. Appl. Phys. 85 (1999) 3314.
[16] R. Mota, D. Galvao, S.F. Durrant, M. Moraes, S. Dantas, M. Cantao, Thin Solid Films 270 (1995) 109.
[17] C. Rau, W. Kulish, Thin Solid Films 249 (1994) 28.
[18] H. Kato, N. Kashio, Y. Ohki, K.S. Seol, T. Noma, J. Appl. Phys. 93 (2003) 239.