Thin Film Characterization on Refractive Index of PECVD SiO_2 Thin Films

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ABSTRACT

Silicon oxide thin films have been deposited by plasma-enhanced chemical vapor deposition in SiH4 and N2O plasma along the variation of the gas flow ratio. Optical emission spectroscopy was employed to monitor the plasma and ellipsometry was employed to obtain refractive index of the deposited thin film. The atomic ratio of Si, O, and N in the film was obtained using XPS depth profiling. Fourier Transform Infrared Spectroscopy was used to analyze structures of the films. RI decreased with the increase in N2O/SiH4 gas flow ratio. We noticed the increase in the Si-O-Si bond angles as the N2O/SiH4 gas flow ratio increased, according to the analysis of the Si-O-Si stretching peak between 950 and 1,150 cm-1 in the wavenumber. We observed a correlation between the optical emission intensity ratio of (ISi+ISiH)/IO. The OES intensity ratio is also related with the measured refractive index and chemical composition ratio of the deposited thin film. Therefore, we report the added value of OES data analysis from the plasma related to the thin film characteristics in the PECVD process.

Key Words : Plasma-Enhanced Chemical Vapor Deposition, Thin Films, Gas Flow Ratio, Refractive Index, Optical Emission Spectroscopy

1. Introduction

Silicon dioxide thin films are widely used in the semiconductor industry for applications such as passivation, interlayer dielectric, gate dielectric, and capacitor for memory devices. Processes such as diffusion and deposition are employed to form Silicon dioxide thin films. Plasma-enhanced deposition is widely used in semiconductor and display manufacturing processes due to its advantage of low deposition temperatures [1]. The quality of SiO_2 films deposited using plasma depends on process variables such as chamber pressure, substrate temperature, RF power, process gas flow rate, and electrode distance [2-3]. To satisfy the required thin film properties, it is essential to understand the relationship between the thin film material properties and the plasma state, and to optimize the process according to the desired characteristics based on the understanding of process variables and plasma conditions.

Among the various physical, chemical, and mechanical properties of thin films, the refractive index (RI) is a good figure of merit for the physical property that includes both the chemical properties related to the material's bonding structure and the mechanical properties related to density. A low refractive index is required to increase the light conversion efficiency in anti-reflective coatings and enhance the light extraction efficiency of light-emitting diodes [4]. For interlayer dielectric materials, low dielectric constant materials should be used to reduce RC delay [5]. RI is inversely proportional to the square root of the dielectric constant, and while the dielectric constant can be determined

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by measuring the change in capacitance using electrical methods, the refractive index can be measured using physical methods such as ellipsometry or a prism coupler. However, the methods have the disadvantage of requiring the use of measuring instruments after the process has been performed.

In this study, noting that the refractive index of thin films is related to their chemical composition, we conducted research on in-situ monitoring of process plasmas using optical emission spectroscopy (OES) and investigated the possibility of elucidating the correlation between the chemical composition of thin films. OES converts the light source generated by ions and radicals existing in the plasma into an absorption spectrum, monitoring the intensity of the emitted spectrum observed at a specific wavelength, and observes changes in the relevant chemical species [1]. OES is non-intrusive, allows for in-situ process monitoring, enables rapid diagnostics, and is ideal for industrial use. Currently, OES is widely used as an end point detector (EPD) in the etching process commercially. However, it is rarely used for deposition processes in the industry, such as predicting deposited film characteristics. Nevertheless, research on monitoring deposition processes to locate defects or study the thickness of thin films is underway, and significant conclusions are being drawn in relation [6-7].

In Dao's study, the N_2O/SiH_4 gas flow ratio was set within the range of 1/6-20/1, yielding a refractive index range of 2.64-1.47 [3]. In this study, to obtain a lower refractive index range than that derived from previous studies, the deposition was carried out by modifying the N_2O/SiH_4 gas flow ratio range to 20/1-50/1. To investigate the effect of the plasma state during the deposition process on the composition and refractive index of the thin film, in-situ plasma states were observed using OES. The refractive index of the deposited film was measured using ellipsometry, and the chemical bonding and composition analysis were performed with Fourier Transform Infrared Spectroscopy (FT-IR) and X-ray Photoelectron Spectroscopy (XPS). The changes in the chemical composition and refractive index of the SiO_2 thin film with respect to the N_2O/SiH_4 gas flow ratio were examined. The correlation between the OES $(I_{Si}+I_{SiH})/I_O$ Intensity ratio and these changes was studied.

Table 1. SiO_2 Deposition Process recipe

Experiment	Unit	Value
Pressure(mTorr)	mTorr	2,250
Power(W)	Watt	400
N_2O flow rate	sccm	4,000
SiH_4 flow rate	sccm	200-60
N_2 flow rate	sccm	3,000
Temperature	℃	400
Time	second	45

	Run1	Run2	Run3	Run4	Run5	Run6	Run7
N_2O (sccm)	4,000						
SiH_4 (sccm)	200	180	160	140	120	100	80
N_2 (sccm)	3,000						

2. Experiment

In this experiment, SiO_2 films were deposited using a 300 mm capacitively coupled plasma (CCP)-PECVD system operating at 13.56 MHz. In order to investigate the refractive index of SiO_2 films according to the N_2O/SiH_4 gas flow ratio, the deposition was carried out in a total of 7 separate unit processes (Runs). The recipe for SiO_2 deposition is as follows; $SiH_4 + 2N_2O \rightarrow SiO_2 + 2H_2 + 2N_2$ [8]. Table 1 is the SiO_2 Process recipe. Ellipsometry was used to measure the refractive index, n of the film. To analyze the elemental composition and chemical structure of the film, FT-IR (Fourier Transform Infrared Spectroscopy) was used. The element ratio of the thin film was confirmed through the results of XPS (X-ray Photoelectron Spectroscopy) analysis using the Depth profiling method.

3. Results and Discussion

Fig. 1 is a graph of the refractive index (RI) as a function of the gas flow rate ratio, γ (N_2O/SiH_4). The SiO_2 deposition was carried out by increasing the gas flow ratio from Run1 to Run7. The measurements in Table 2 show that the RI decreased as the gas flow ratio was increased.

XPS measurements were conducted to examine the elemental composition. To analyze the data obtained from these measurements, the O1s peak binding energy was examined near 532 eV, Si2p near 103 eV, and N1s near 398 eV. As a result, as shown in Table 3, the trend indicated that

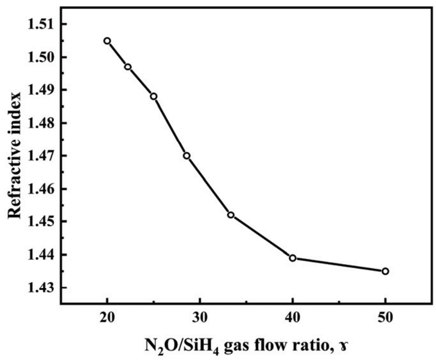

Fig. 1. Refractive index, n of silicon oxide deposited as a function of N_2O/SiH_4 gas flow ratio, ɤ.

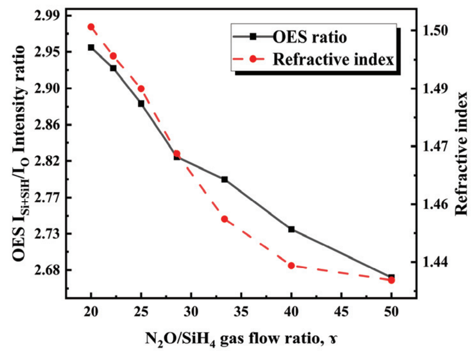

Fig. 2. Correlation between $I_{Si}+I_{SiH}/I_O$ OES intensity ratio and the refractive index, n, as function of N_2O/SiH_4 gas flow ratio at 400 W, and 2250mTorr.

Table 2. Reflective Index, n table

Run time	Reflective index
Run 1	1.505
Run 2	1.497
Run 3	1.488
Run 4	1.470
Run 5	1.452
Run 6	1.439
Run 7	1.435

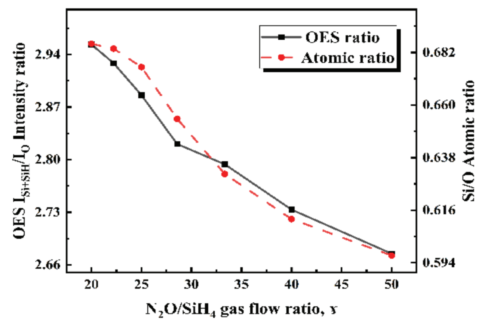

Fig. 3. Correlation between OES intensity ratio and Si/O Atomic ratio, as function of N_2O/SiH_4 gas flow ratio at 400 W, and 2250mTorr.

Table 3. XPS Analysis Results

Name / Run	Atomic (%)		
	Si	O	N
Run 1	38.36	55.95	5.69
Run 2	38.87	56.86	5.11
Run 3	36.62	57.14	4.24
Run 4	38.11	58.25	3.64
Run 5	37.61	59.59	2.80
Run 6	37.24	60.82	1.93
Run 7	37.38	62.61	0

the O content in the film increased as the SiH_4 flow rate decreased, while Si showed a similar trend, and N gradually decreased until it was no longer detectable.

The relationship between the $(I_{Si}+I_{SiH})/I_O$ OES intensity ratio and the elemental proportion of the film measured by XPS was analyzed. For the OES intensity, the average value of the intensity that appeared during the process time was used. As shown in Fig. 2, it was observed that the decrease in the chemical composition ratio with respect to increasing ɤ and the OES intensity ratio are proportional. The relationship between the $(I_{Si}+I_{SiH})/I_O$ OES intensity ratio and RI was also analyzed. As shown in Fig. 3, it was confirmed that the decrease in RI with respect to increasing ɤ and the OES intensity ratio are proportional. In order to verify the correlation between the refractive index, chemical composition ratio, and OES intensity ratio, the Pearson correlation coefficient was calculated. The correlation between the refractive index (RI) and optical emission spectroscopy (OES) was found to be 0.9842, and the correlation between the chemical composition ratio and OES was 0.9899, a very high correlation.

To observe the bonding of the elements, the deposited films were measured using FT-IR. From Run1 to Run7, as the N_2O/SiH_4 gas flow ratio increased, the Si-O-Si stretching was examined in the wavelength range of 950 cm^{-1} to 1150 cm^{-1} to observe changes in Si-O-Si bonding. As a result, as shown in Fig. 4, the stretching banding shifted from 950 cm^{-1} to 1300 cm^{-1}. This is related to the change in the distribution of the Si-O-Si angle in the SiO_2 film. In the case

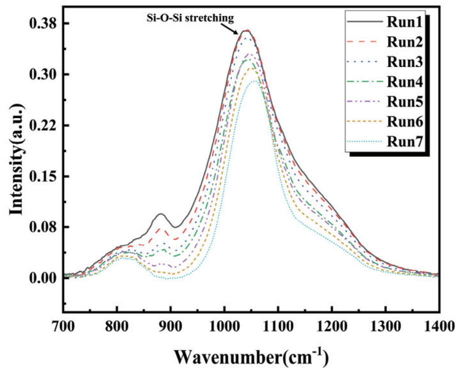

Fig. 4. FT-IR transmittance spectrum in the wavenumber of 700 - 1400 cm^{-1} varying N_2O/SiH_4 gas flow ratio, ɤ.

of SiO_2 films, it is known that the shift of the stretching peak to a higher wavenumber occurs as the Si-O-Si bond angle increases [9]. It is known that as the Full-width at half maximum (FWHM) of the stretching peak decreases, the Si-O-Si bond angle increases [10]. In addition, the shift of the stretching peak to a higher wavenumber indicates a decrease in film density; thus, as ɤ increases, the bond angle increases, the density decreases, and the refractive index decreases [11-12].

Although measuring film density using X-ray Reflectivity (XRR) would provide a reliable analysis to confirm the decrease in film density due to the shift of the stretching peak to a higher wavenumber, it was not possible to perform XRR analysis due to the limited research environment in the university at present.

4. Conclusion

In this study, SiO_2 films were deposited using a PECVD system. The refractive index of the deposited SiO_2 was measured using ellipsometry, and the elemental composition ratio of the film was obtained through XPS. It was found that as the N_2O/SiH_4 gas flow ratio increased, the oxygen content in the film decreased, and the refractive index also decreased. The Si-O-Si stretching peak was analyzed using FTIR measurement data. It was confirmed that as the N_2O/SiH_4 gas flow ratio increases, the Si-O-Si bonding angle increases and the density decreases, leading to a decrease in the refractive index.

A strong correlation between the OES $(I_{Si}+I_{SiH})/I_O$ intensity and refractive index as well as the OES $(I_{Si}+I_{SiH})/I_O$ intensity and chemical composition ratio was confirmed. The correlation coefficient with the refractive index was 0.9842, and the correlation coefficient with the chemical composition ratio was 0.9898, indicating a high correlation. Based on these results, the possibility of utilizing in-situ plasma measurement and diagnostic technologies using OES in the PECVD process can be increased. Moreover, by securing a large amount of data and applying artificial intelligence-based data analysis

algorithms, it is expected to contribute to PECVD process monitoring and diagnostic technology.

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