Characteristics of a Multilayer $SiO_x(CH)_yN_z$ Film Deposited by Low Temperature Plasma Enhanced Chemical Vapor Deposition Using Hexamethyldisilazane/Ar/N$_2$O

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$SiO_x(CH)_yN_z$ films were deposited at room temperature using plasma enhanced chemical vapor deposition (PECVD) with a gas mixture of hexamethyldisilazane [HMDS, $Si_2NH(CH_3)_6$]/Ar/N$_2$O. The characteristics of those films with increasing N$_2$O were investigated. When no N$_2$O was used, the film showed organic characteristics with a Si/O composition ratio of 2 and a large concentration of –CH$_x$ and N–H in the deposited film. However, with increasing N$_2$O flow rate, oxygen-rich and transparent SiO$_2$-like inorganic thin films could be obtained with a Si/O composition ratio of 0.5 and a lower –CH$_x$ and N–H in the deposited film. By turning on-and-off the N$_2$O gas flow during $SiO_x(CH)_yN_z$ deposition, a multi-layer thin film consisting of an organic Si(CH)$_x$-like film/inorganic SiO$_2$-like thin film, which can be applied to the thin film passivation for organic devices could be successfully deposited.   [DOI: 10.1143/JJAP.45.8430]

KEYWORDS: HMDS, SiO$_2$, diffusion barrier, PECVD, N$_2$O

1. Introduction

The deposition of thin film materials such as SiO$_2$, Si$_3$N$_4$, etc. at low substrates temperatures[1,2] is attracting increasing attention for their potential applications in areas such as organic thin film transistors (OTFTs) and organic light emitting diodes (OLEDs) in the next generation of flat panel display (FPD) devices,[3,4] and as dielectric materials for insulation, waveguiding, device passivation, etc, in solid state electronic and optoelectronic devices.[5,6] In particular, the use of flexible polymer substrates instead of sodalime glass substrates for the next generation FPD, which can reduce the weight, thickness, and cost of large area FPD, requires an extensive study of the transparent diffusion barriers for polymer substrates. One of the major problems of the polymer substrates as well as organic-based devices is the short device lifetime caused by the permeation of H$_2$O and O$_2$ during exposure to air.[7,8]

Previous studies[9,10] have shown that the application of a multi-layer thin film consisting of parylene and plasma-enhanced chemical vapor deposition (PECVD) SiO$_2$ or SiO$_x$N$_y$, i.e., a multilayer thin film composed of organic material and inorganic thin films, can be helpful in improving the efficiency of the diffusion barrier. However, in order to form a multilayer thin film composed of parylene and PECVD SiO$_2$ or SiO$_x$N$_y$, different process chambers need to be used to deposit the organic and inorganic thin films in order to prevent cross-contamination. However, the formation of a multi-layer thin film in separate process chambers increases the process time and creates a sharp interface between the inorganic and organic materials, which increases the possibility of delamination.

Therefore, in this study, a multilayer organic and inorganic thin film composed of $SiO_x(CH)_yN_z$ was fabricated in the same chamber using a same organic precursor such as hexamethyldisilazane (HMDS) and by adding/removing the oxidizing gas in the gas mixture (e.g., N$_2$O) during film deposition using PECVD. The characteristics of the inorganic and organic materials and the multilayer thin film were investigated as a possible application to a thin film passivation layer. The PECVD technique was used to deposit the multilayer because it has flexibility in varying the chemical composition and allows the industrial-scale deposition of a high quality barrier material with good uniformity and adhesion to the substrate in addition to allowing deposition at lower temperatures.[11–13] By depositing a multilayer thin film using the above method, it is believed that not only can the processing time be shortened but the mechanical properties and optical properties of the deposited thin film can also be improved by forming a graded interface between organic thin film and inorganic thin film instead of a sharp interface.

2. Experimental Methods

Figure 1 shows a schematic diagram of the PECVD reactor used to deposit the multilayer thin film composed of organic and inorganic materials at a low temperature. As a plasma source, a planar-type inductively coupled plasma (ICP) source made from a 3-turn copper coil, 210 mm in diameter, and operated at 300 W of 13.56 MHz was used for the high dissociation of gas molecules. The substrate, 110 mm in diameter, was biased at -100 V using a separate 13.56 MHz rf power source, and was maintained at a temperature $< 40\,°C$ using a chiller. The gas mixtures were supplied to the reactor (260 mm inner diameter) using a gas ring located on the top of the chamber. The liquid source used for silicon was HMDS, which purchased from Sigma-Aldrich with a purity of 99.9%. The HMDS was delivered to the chamber by heating the HMDS liquid source at a fixed temperature of 50 °C and by carrying it into the deposition chamber through a piping system heated to 80 °C. The gas mixture consisting of HMDS/Ar was used to deposit the organic Si(CH)$_x$-like film, and HMDS/Ar/N$_2$O was used to deposit the inorganic SiO$_2$-like material. In order to optimize the characteristics of the inorganic thin film, the N$_2$O flow rate was varied from 0 to 40 sccm while the other process parameters, such as the HMDS flow and Ar flow rates, were maintained at 6 and 75 sccm, respectively. Table I shows the operating conditions for depositing the Si-based organic and inorganic materials are described. The multilayer organic
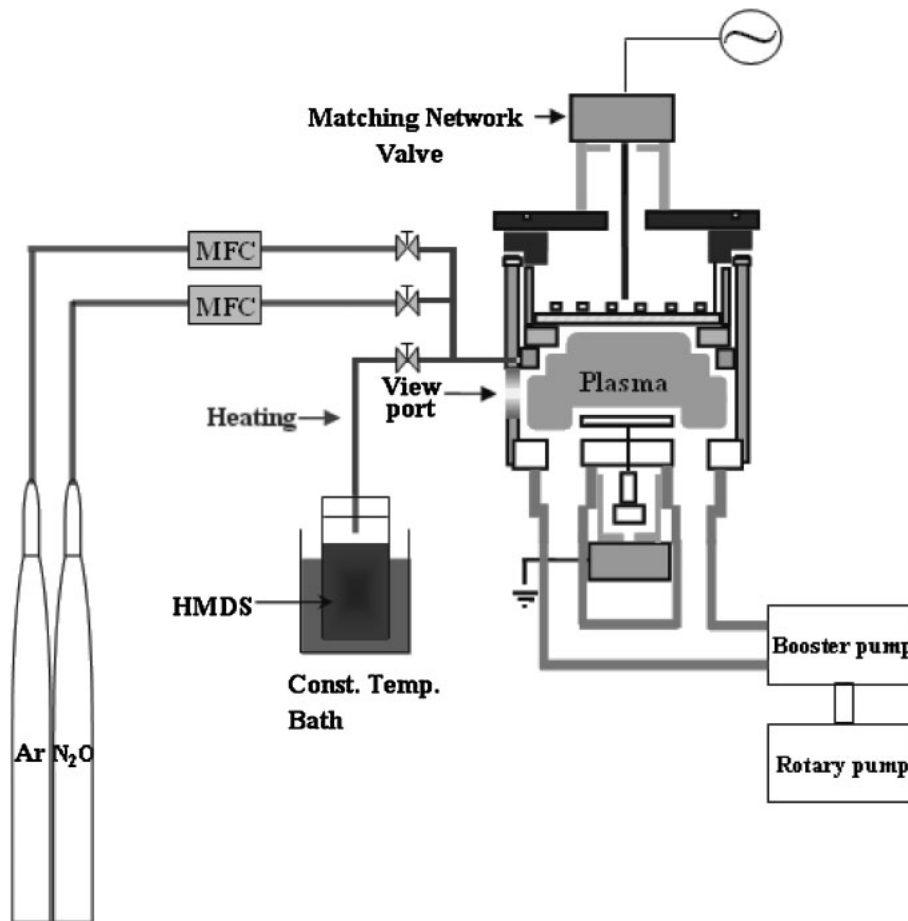
Fig. 1.   Schematic diagram of an ICP-type PECVD apparatus with a bubbling system of HMDS used in this study.

Table I.   Process parameters used in the deposition of $SiO_x(CH)_yN_z$ in this experiment.

Substrate	Si wafer, PES
Gas chemistry	$HMDS + Ar + N_2O$
Deposition temperature	Room temperature
Source power (W)	300
Bias voltage (V)	-100
Bubbler temperature (°C)	50
Delivery line temperature (°C)	80
Flow rate of HMDS (sccm)	6
Flow rate of Ar (sccm)	75
Flow rate of N_2O (sccm)	0–40

Fig. 2.   Deposition rate and refractive index of the $SiO_x(CH)_yN_z$ films measured as a function of the N_2O flow rate. Deposition conditions: HMDS 6 sccm, Ar 75 sccm, 300 W of rf power, and -100 V dc bias voltage, and the substrate temperature 40 °C.

and inorganic thin film using $HMDS/Ar/N_2O$ was deposited by turning the N_2O gas flow on and off during deposition.

The thickness of the deposited film was measured using a step profilometer (Tencor. Alpha step 500), and the composition and the chemical bonding states of the film were measured by X-ray photoelectron spectroscopy (XPS; Thermo Electronics, Multilab ESCA 2000) and Fourier transform infrared spectrometry (FT-IR; Bruker IFS-66/S), respectively. The refractive index and optical transmittance of the deposited materials were measured using an ellipsometer (L-117, Gaertner) with a 633 nm He–Ne laser light source and by ultraviolet–visible (UV–vis) spectroscopy (Scinco, UV S-2100), respectively. The cross section of the
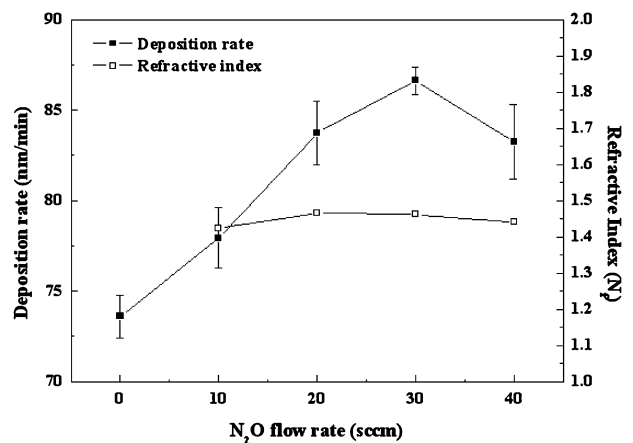
multilayer thin film was observed by field emission scanning electron microscopy (FE-SEM; Hitachi, S-4700).

3.   Results and Discussion

Figure 2 shows the deposition rate and the refractive index of the $SiO_x(CH)_yN_z$ deposited by inductively coupled PECVD using $HMDS/Ar/N_2O$ gas mixtures, as a function of the N_2O flow rate from 0 to 40 sccm whilst maintaining the HMDS and Ar flow rates at 6 and 75 sccm, respectively.

The process pressure ranged from 115 to 140 mTorr. The RF power to the plasma source and the dc-bias voltage to the substrate were also maintained at 300 W and −100 V, respectively. The sample used in the experiment was a p-type ⟨100⟩ wafer, and during deposition, the sample temperature was maintained at <40 °C. As shown in Fig. 2, when HMDS/Ar was used without N_2O, the deposition rate was approximately 73.6 nm/min. the deposition rate was increased to 86.6 nm/min by adding and increasing N_2O up to 30 sccm. A further increase in the N_2O flow rate slightly decreased the deposition rate to 83.2 nm/min. The increase in the deposition rate with increasing N_2O flow rate in HMDS/Ar/N_2O appears to be related to the increased level of silicon incorporation in the film as a result of the formation of less volatile Si–O bonds with oxygen from the decomposed N_2O ($N_2O + X^* \rightarrow NO + O, NO + X^* \rightarrow N + O$)[14] through the removal of C, H, N in the HMDS. However, the slight decrease in the deposition rate observed at 40 sccm appears to be related to the saturation of the reaction between HMDS and oxygen and the further removal of organic impurities such as –CH_x incorporated in the film.

Figure 2 shows the refractive index of the $SiO_x(CH)_yN_z$ materials deposited as a function of the N_2O flow rate. As shown in the figure, the refractive index increased from approximately 1.42 to 1.46 when the N_2O flow rate was increased from 10 to 20 sccm, and a further increase in the N_2O flow rate to 40 sccm slightly decreased the refractive index. However, the refractive index was in the range of 1.45 ± 0.01. It was difficult to measure the refractive index of the material deposited with HMDS/Ar only but it is believed that the refractive index of the material deposited with HMDS/Ar only would be lower than that deposited with HMDS/Ar/N_2O by having the characteristics of an organic thin film. The refractive index of 1.45 ± 0.01 is similar to the refractive index of SiO_2-like inorganic film. Therefore, the deposited film changed to a SiO_2-like thin film with increasing N_2O flow rate higher than 20 sccm.

Figure 3 shows the FTIR data of the films deposited under the conditions shown in Fig. 2. The thickness of the deposited films on a p-type ⟨100⟩ silicon wafer was maintained at 300 nm. As shown in the figure, the film deposited with HMDS/Ar showed a large peak at 1020 cm^{-1}, which was
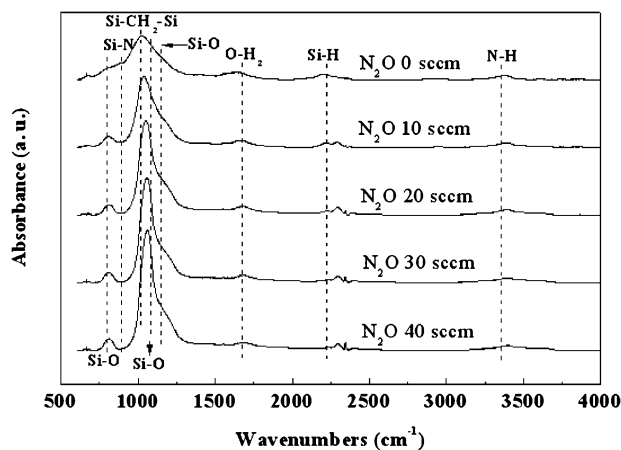

Fig. 3. FR-IR spectra of the $SiO_x(CH)_yN_z$ films as a function of the N_2O flow rate. The deposition conditions are the same as those shown in Fig. 2.

Table II. Structure formula of HMDS and the relevant bond energies.

Structure formula (M = CH$_3$)	Bond energies (eV)	
	Si–C	3.12
	Si–N	3.42
	Si–H	3.35
	N–H	4.05
	C–H	4.31
	H–H	4.52

assigned to Si–CH_2–Si bonding, mixed with small peaks assigned to Si–N bonding at 900 cm^{-1} and Si–O bonding at 1070 cm^{-1}.[15] This indicates the characteristics of a Si-based organic film. In addition, a peak at 3373 cm^{-1} assigned to N–H stretching vibration, a peak at 2208 cm^{-1} assigned to Si–H bonding, and a peak at 800.4 cm^{-1} assigned to Si–O bonding were also observed. O–H_2 bonding possibly related to the adsorption of H_2O on the film was observed at 1643 cm^{-1}.[16] Table II shows the molecular structure of HMDS and the binding energies of the bonds in HMDS. The observed bonds, such as Si–CH_2–Si, Si–N, and N–H, were attributed to undissociated HMDS. By increasing the N_2O flow to the gas mixture, the peak heights for the Si–CH_2–Si, Si–N, and Si–H bonds with a concomitant increase in the peak height for Si–O bonding. Therefore, a sharp peak at 1070 cm^{-1} assigned to Si–O bonding could be observed at 40 sccm of N_2O. In addition, the peak assigned to the N–H stretching vibration at 3373 cm^{-1} also decreased with increasing N_2O flow rate. The decrease in the peak heights related to Si–CH_2–Si, Si–N, and N–H bonds with increasing N_2O flow rate was attributed to the replacement of low energy bonds such as Si–C (binding energy: 3.12 eV), Si–H (binding energy: 3.35 eV), Si–N (binding energy: 3.42 eV), and N–H (binding energy: 4.05 eV)[17,18] with more stable Si–O bonds (binding energy: 8.3 eV)[19] as a result of the higher number of oxygen atoms in the plasma. Therefore, by increasing N_2O flow rate, a more SiO_2-like inorganic film could be obtained with fewer impurities such as C, H, and N.

A multilayer thin film was formed by depositing $Si(CH)_x$-like organic and SiO_2-like inorganic films alternatively by turning on and off the N_2O gas flow during PECVD with HMDS/Ar/N_2O. Thirty sccm of N_2O was used for depositing the inorganic film, with the other PECVD deposition conditions being the same as those shown in Table I. The thickness of each organic and inorganic layer was maintained at 1.2 µm and 300 nm, respectively. Figure 4(a) shows a cross-sectional SEM image of the grade multilayer composed of total four layers on a silicon wafer. As shown in the figure, the cross-section of the organic film shows a rough surface while that of the inorganic film shows a smooth surface. From the SEM image, there was no clear interface between the organic and inorganic layers indicating a graded interface due to the slow decrease and increase in N_2O flow when turning on and off N_2O flow during deposition. Figure 4(b) shows a cross-section SEM image of a typical multilayer composed of two SiO_2 layers and one organic layer on the silicon wafer. The thickness of each organic and inorganic film was maintained at 1.2 µm and 600 nm, respectively, under the same process conditions used for the grade multilayer. However, each layer was
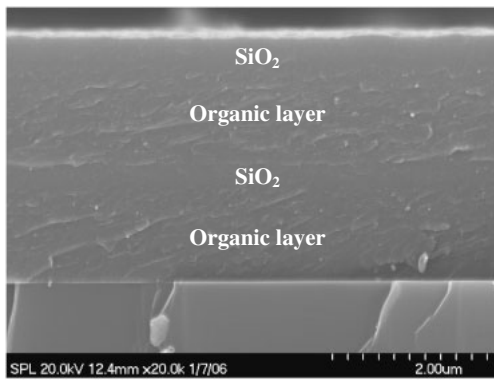
(a)
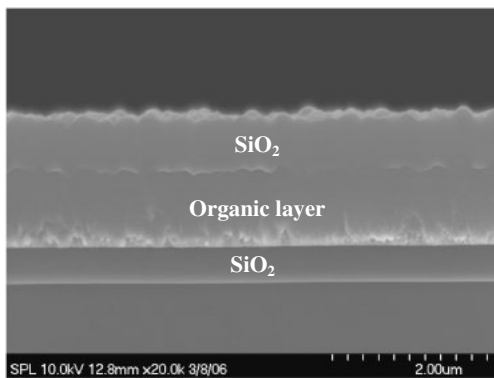
(b)

Fig. 4. SEM micrographs for (a) a 3 μm thick grade multilayer and (b) 2.2 μm thick typical multilayer; formed by depositing Si(CH)$_x$-like organic thin film and SiO$_2$-like inorganic films using HMDS/Ar/N$_2$O. 30 sccm of N$_2$O was used for the inorganic film. The other deposition condition is as follows: HMDS 6 sccm, Ar 75 sccm, 300 W of rf power, and −100 V dc bias voltage.

Fig. 5. Optical transmittance spectra of the grade multilayer and typical multilayer thin film consisting of a 140 nm organic layer [Si(CH)$_x$-like film]/86 nm inorganic layer (SiO$_2$ like film)/... on a PES (200 μm) substrate. The deposition conditions are the same as those reported in Fig. 4.

Fig. 6. XPS composition depth profile of the multilayer thin film composed of a 300 nm inorganic layer (SiO$_2$-like film)/1.2 μm organic layer [Si(CH)$_x$-like film]/300 nm inorganic layer (SiO$_2$-like film) on a silicon wafer. The deposition conditions are the same as those shown in Fig. 4.

deposited separately to obtain the multilayer. As shown in Fig. 4(b), in the case of the typical multilayer, sharp interfaces (distinctive line) were clearly seen between the SiO$_2$ and organic layers while the SEM micrograph of the graded multilayer shown in Fig. 4(a) did not show such a sharp interfaces. The thickness of the graded interface zone was estimated to be approximately 10.7 nm.

A graded interface is believed to decrease the reflection of light at the interface and increase the adhesion properties compared with a sharp interface. Figure 5 shows the optical transmittance spectra of the graded multilayers and typical multilayers deposited on 200 μm thick poly(ether sulfone) (PES). Two multilayers were deposited with the same thickness with the deposition conditions being the same as those shown in Fig. 4. The thicknesses of each organic film and each inorganic film were maintained at 140 and 86 nm, respectively. As shown in the figure, the optical transmittance of the typical multilayers were lower than those of the graded multilayers, which was attributed due to the decrease in light reflected at the graded interface.

Figure 6 shows the composition and XPS depth profile of the multilayer thin film (two inorganic thin film/one organic thin film on Si) deposited under the conditions shown in Fig. 4. The components detected were Si, C, N, and O. Even though the type of bonding related to Si–H was detected by FTIR, as shown in Fig. 3, H could not be analyzed by
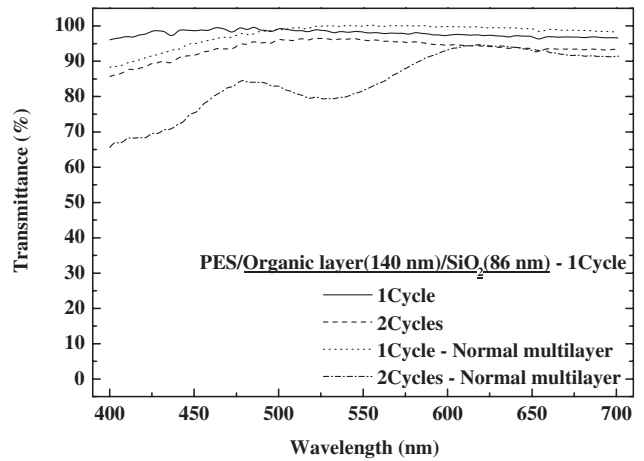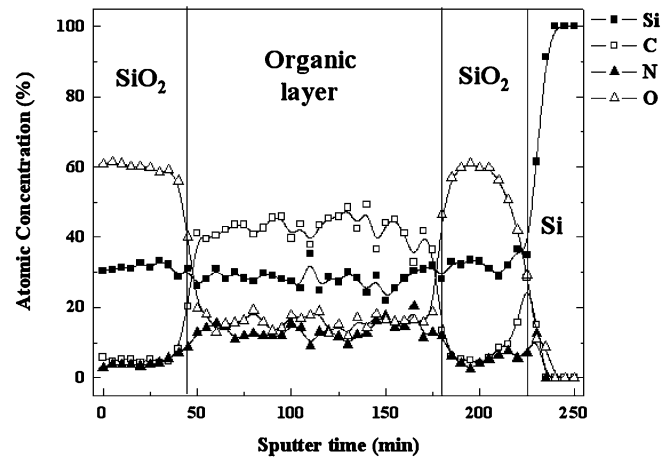
XPS due to the detection limit of the XPS. The atomic composition for the organic layer without considering the possible H content in the film was Si 32%, O 15%. C 40%, N 13% and, that for the inorganic layer was Si 32%, O 60%, C 5%, N 3%, which is similar to the FTIR results shown in Fig. 3. Therefore, Si(CH)$_x$-like and SiO$_2$-like material were deposited as the organic and the inorganic layers, respectively. As shown in the figure, the compositions of the alternating inorganic layers were similar. In addition, the compositions of the organic and inorganic materials remained similar throughout the thickness of each layer. The interface appeared to show a graded interface with a gradual change in composition. However, this was not completely clear due to the sputter mixing of materials during the depth profile operation of XPS.

4. Conclusions

In this study, multilayer thin films consisting of organic

and inorganic thin films was fabricated at a low temperature by inductively coupled PECVD using HMDS/Ar/N_2O and by adding/removing N_2O in the gas mixture alternatively during film deposition. The characteristics of the inorganic and organic materials and the multilayer thin film were investigated for possible applications to a thin film passivation layer. The result showed that, with increasing N_2O in the HMDS/Ar/N_2O gas mixture, the deposited film showed less C, N, and H and more O due to the replacement of Si–C, Si–H, Si–N, and N–H bonds with higher bonds with a binding energy such as Si–O. The film deposited with HMDS (6 sccm)/Ar (75 sccm) showed the characteristics of a Si(CH)$_x$-like organic material while the film deposited with HMDS (6 sccm)/Ar (75 sccm)/N_2O (>30 sccm) showed the characteristics of a SiO_2-like inorganic thin film. A multi-layer thin film consisting of Si(CH)$_x$-like organic and SiO_2-like inorganic films with a possible graded interface was obtained when deposited using HMDS/Ar/N_2O and by turning the N_2O on and off during inductively coupled PECVD. It is expected that this material will be applicable to thin film passivation.

Acknowledgements

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