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SiO_xN_y thin film deposited by plasma enhanced chemical vapor deposition at low temperature using HMDS–O_2–NH_3–Ar gas mixtures

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Abstract

In this study, SiO_xN_y thin film was deposited by plasma enhanced chemical vapor deposition at the temperature lower than 40 °C using hexamethyldisilazane (HMDS)/Ar while varying the ratio of O_2/NH_3. And, its physical and chemical characteristics of the deposited SiO_xN_y as a diffusion barrier to water permeation applied to organic thin film transistors (OTFTs) were investigated. When oxygen ratio (R) in O_2/NH_3 ($R=O_2/(O_2+NH_3)$) was lower than 0.3, due to the high remaining binding states such as $-CH_x$ and N–H in the deposited film, the deposited film was soft and easily peeled off. With increasing R, oxygen-rich, hard, and transparent SiO_xN_y thin film was deposited with lower $-CH_x$ and N–H. When a thin film composed of parylene (100 nm)/SiO_xN_y (60 nm)/parylene (100 nm) was formed on the polyethersulfone (PES, 200 μm) film with SiO_xN_y deposited with $R=0.5$, water vapor transmission rate (WVTR) of 0.3 gm/(m^2 day) could be obtained. It is believed that, by using a multilayer SiO_xN_y structure, the WVTR required for OTFTs ($\sim 10^{-2}$ gm/(m^2 day) could be obtained.
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1. Introduction

Recently, transparent diffusion barrier materials such as inorganic material films are receiving much attention in the flat panel display (FPD) industries for the passivation of organic thin film transistors (OTFTs) and organic light emitting diodes (OLEDs) [1–3]. In addition, the use of flexible polymer substrates instead of soda lime glass substrates for the next generation FPD in order to reduce the weight, thickness, and cost of large area FPD requires a study of the transparent diffusion barriers to the polymer substrates. It is due to the fact that one of the major problems of the polymer substrates in addition to the organic-based devices is the short device lifetime caused by the permeation of H_2O and O_2 during the exposure to the air [4,5].

Various permeation barrier materials and various deposition methods are intensively investigated for the passivation of OTFTs and OLEDs [6–8]. Among the various materials, SiO_xN_y widely used for the solid state electronic and optoelectronic devices [9–12] can be applicable due to its diffusion barrier property in addition to its scratch hardness. SiO_xN_y film is currently deposited by various methods [13–15], however, the plasma enhanced chemical vapor deposition (PECVD) technique is particularly interesting due to the flexibility in varying chemical composition and deposition rate by changing the deposition parameters at low temperatures [16–18].

In this study, using $HMDS/NH_3/O_2/Ar$ gas mixtures, SiO_xN_y thin film was deposited on plastic substrates at a low temperature using a PECVD method and its properties were investigated as a thin film diffusion barrier to water permeation. HMDS was used as the precursor of Si because, as a liquid, it is relatively safe, noncorrosive, readily available at high purity, and has been widely accepted in the integrated circuit industry as a photoresist adhesion promoting agent [19]. Also, it is chemically stable compared to other silicon precursors such as SiH_4, SiH_xCl_y, etc. [20].

2. Experimental

Fig. 1 shows the schematic diagram of the PECVD reactor used in this experiment for the deposition of SiO_xN_y at a low temperature. As the plasma source, a planar-type inductively coupled plasma (ICP) source made of a 3-turn copper coil and

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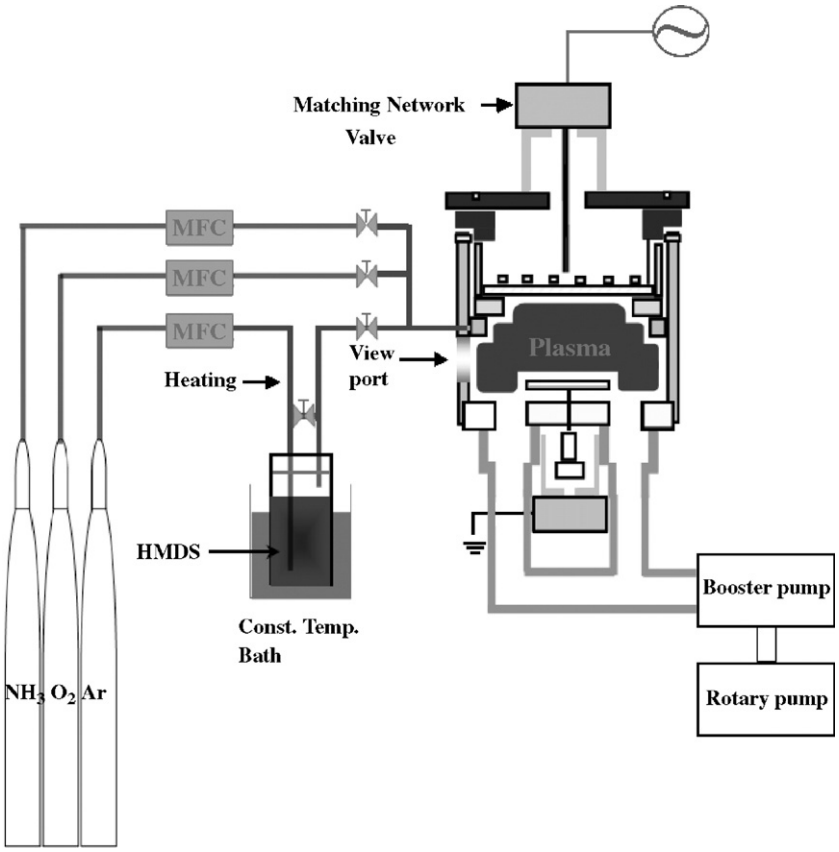


Fig. 1. Schematic illustration of an ICP-type PECVD apparatus with a bubbling system of HMDS used in this study.

operated at 300 W of 13.56 MHz was used for the high dissociation of gas molecules. The substrate was maintained at the temperature lower than 40 °C using a chiller and biased at −150 V using a separate 13.56 MHz rf power. Gas mixture was supplied to the reactor using a gas ring located on the top of the chamber. The liquid source for silicon was hexamethyldisilazane (HMDS, $Si_2NH(CH_3)_6$), provided by Acros organics with a purity of 98%. The gas mixture composed of HMDS/NH_3/O_2/Ar was used to deposit SiO_xN_y. In this gas mixture, HMDS was delivered to the chamber by heating the HMDS liquid source at a fixed temperature of 50 °C and carried into the deposition chamber by a piping system heated to 80 °C. The flow rates of HMDS (5–15 sccm) and the ratio of $O_2/(NH_3+O_2)$ at 20 sccm of NH_3+O_2 were varied for the optimization of the SiO_xN_y film. Ar flow rate was maintained at 75 sccm. The operating conditions for the deposition of SiO_xN_y are described in Table 1. SiO_xN_y was deposited on the silicon wafer to measure the deposition rate and to study the characteristics of the deposited film and also on the 200 μm thick polyethersulfone (PES) to measure the water permeation properties.

The thickness of the deposited film was measured using a step profilometer (Tencor Inc. Alpha-step 500). The chemical compositions and binding states of the deposited SiO_xN_y films were investigated using a X-ray photoelectron spectrometer (XPS, VG Microtech Inc., ESCA2000) and a fourier transform infrared spectrometer (FT-IR, Bruker IFS-66/S, Bruker), respectively. To measure the water permeation property, a multilayer film composed of inorganic SiO_xN_y films and organic parylene films was deposited on PES. The parylene film was deposited by a parylene coater (SCS, Inc., PDS 2010 LABCOTER). The water vapor transmission rate (WVTR) of the multilayer thin film on PES was measured using a WVTR measurement system (MOCON Inc., PERMATRAN-W Model3/33).

3. Results and discussion

Fig. 2 shows the effect of oxygen ratio R ($R=O_2/(O_2+NH_3)$) for 5 sccm of HMDS and the effect of HMDS flow rate for the oxygen ratio of 0.5 in the HMDS/Ar/O_2/NH_3 gas mixture on the deposition rate of SiO_xN_y on Si <100> substrate. Ar flow rate

Table 1
Process parameters used in the SiO_xN_y deposition in this experiment

Substrate	Si wafer, PES
Gas chemistry	HMDS+Ar+O_2+NH_3
	O_2+NH_3=20 sccm, $R=O_2/(O_2+NH_3)$
Deposition temperature	Room temperature
Source power	300 W
Bias voltage	−150 V
Bubbler temperature	50 °C
Delivery line temperature	80 °C
Flow rate of HMDS	5–15 sccm
Flow rate of O_2	2–18 sccm
Flow rate of Ar	75 sccm
Flow rate of NH_3	2–18 sccm

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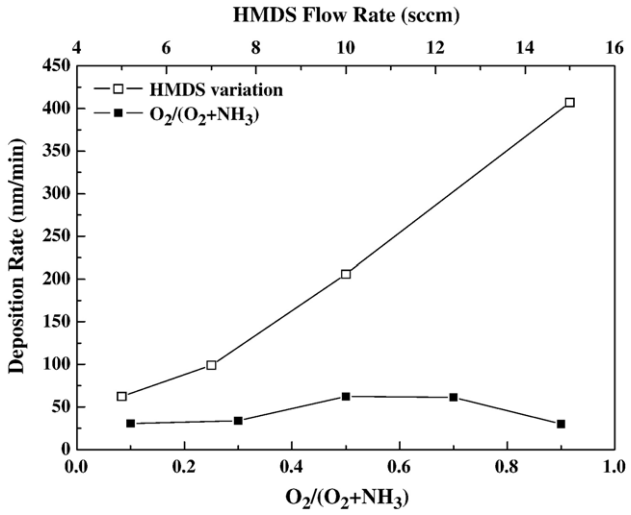


Fig. 2. Deposition rate of SiO_xN_y films measured as a function of oxygen ratio R ($R=O_2/(O_2+NH_3)$) for 5 sccm of HMDS and as a function of HMDS flow rate for the oxygen ratio of 0.5 in the HMDS/Ar/O_2/NH_3 gas mixture. Deposition condition: (HMDS 5 sccm/(O_2+NH_3):20 sccm/Ar 75 sccm), 300 W of the rf power, and −150 V dc bias voltage, and the substrate temperature 40 °C.

was maintained at 75 sccm and total gas flow rate of O_2+NH_3 was maintained at 20 sccm. The working pressure was kept at 160 mTorr and the substrate temperature was maintained less than 40 °C. As shown in the figure, the increase of HMDS flow rate from 5 sccm to 15 sccm while keeping the ratio of $O_2/(O_2+NH_3)$ at 0.5 raised the deposition rate from 62.5 nm/min to 407 nm/min, however, with increasing HMDS, even though the films were transparent; they were softer and easily scratched possibly indicating the increase of –CH bonds such as Si–CH_2–Si, Si–$(CH_3)_x$, etc. in the film [17]. When the oxygen ratio R was varied from 0.1 to 0.9 while maintaining HMDS flow rate at 5 sccm, the film was initially blurry and change color with time, and easily scratched possibly due to the –CH and –NH bonds in the film [17,21]. However, when the R is higher than 0.5, the color of the film became transparent and the film became non-scratchable by a tweezer by the removal of C, H,

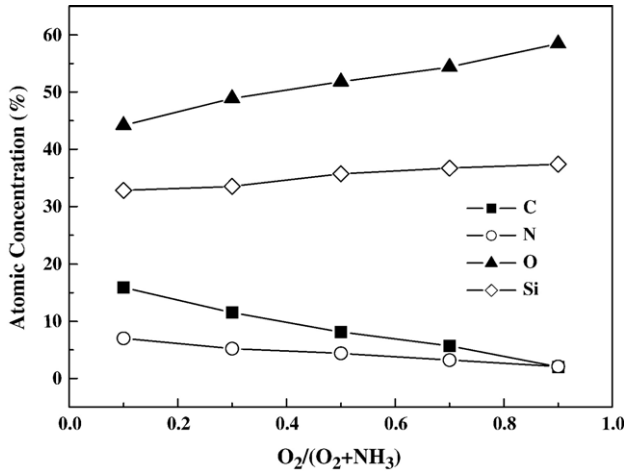


Fig. 3. Atomic concentration of SiO_xN_y films measured by XPS as a function of the O_2 ratio in $O_2/(O_2+NH_3)$. The deposition conditions are the same as those in Fig. 2.

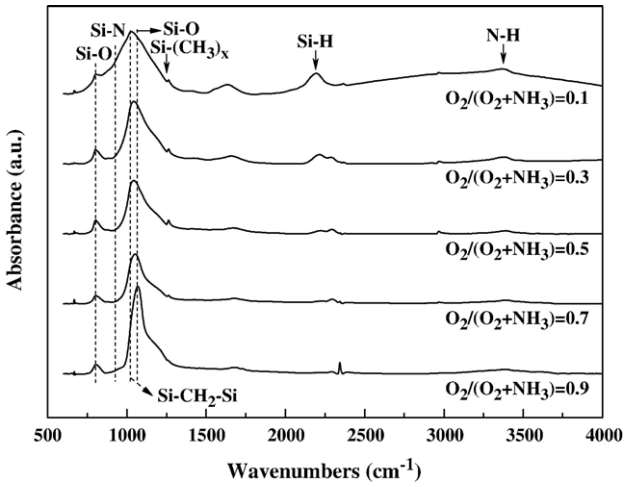


Fig. 4. FT-IR spectra of SiO_xN_y films as a function of the O_2 ratio in $O_2/(O_2+NH_3)$. The deposition conditions are the same as those in Fig. 2.

etc. by oxygen. Highest deposition rate was obtained at $R=0.5$. The reason for the highest deposition rate at $R=0.5$ is not clear at this time.

Fig. 3 shows the atomic composition of the SiO_xN_y films deposited as a function of oxygen ratio. In the figure, due to the difficulty in the measurement of hydrogen contents in the film by XPS, we considered only carbon, nitrogen, silicon, and oxygen detected by XPS. For the measurement, 300 nm thick SiO_xN_y films were deposited on Si <100> substrate. As shown in the figure, with increasing oxygen ratio, the carbon percentage in the film was decreased continuously from 15.9% for $R=0.1$ to 2% for $R=0.9$ while the oxygen percentage was increased from 44.2% to 58.5%. Therefore, by the increase of oxygen ratio, the Si–CH in the film was replaced by oxygen by forming Si–O [22]. In addition, with increasing oxygen ratio, nitrogen percentage in the film was also decreased from 7% for $R=0.1$ to 2.1% for $R=0.9$. Therefore, even with high NH_3

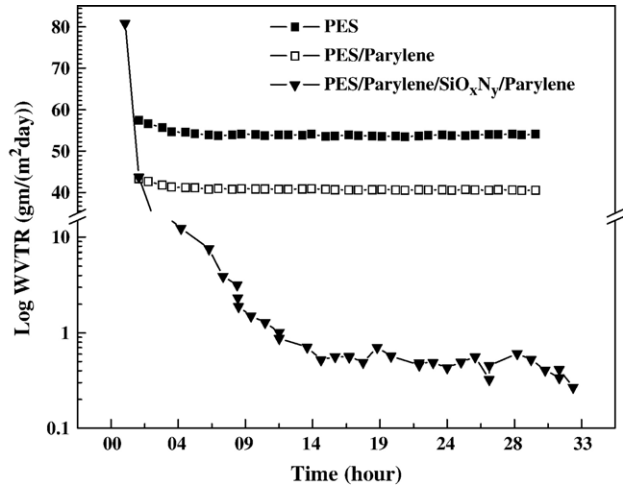


Fig. 5. WVTRs of a multiple layer of PES (200 μm)/parylene (100 nm)/SiO_xN_y (60 nm)/parylene (100 nm). As references, the WVTR of 200 μm thick PES and PES (200 μm)/parylene (800 nm) were also inserted. Deposition condition: HMDS (5 sccm)/(O_2 (10 sccm)/NH_3 (10 sccm)/Ar (75 sccm), 300 W of the rf power, and −150 V dc bias voltage, and the substrate temperature 40 °C.

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content at $R=0.1$, no significant Si–N bonds appears to be formed in the deposited film. In fact, the added NH_3 appears to remain as –NH in the films instead of forming Si–N bonds and Si–N bonds in the film appeared to be replaced to Si–O with increasing oxygen ratio possibly due to the lower binding energy (4.9 eV) of Si–N compared to that (8.3 eV) of Si–O [17,23].

The chemical binding states of the deposited SiO_xN_y films shown in Fig. 3 were further investigated using FTIR and the results are shown in Fig. 4. In the figure, the peaks at 800.4 cm^{-1}, 2194 cm^{-1}, and 3363 cm^{-1} are related to Si–O bonding, Si–H bonding, and N–H bonding, respectively [22]. Also, a broad peak near 1028 cm^{-1} is a merged peak from 900 cm^{-1} of Si–N bonding, 1020 cm^{-1} of Si–CH_2–Si bonding, 1070 cm^{-1} of Si–O bonding, and 1260 cm^{-1} of Si–$(CH_3)_x$ bonding [24,25]. As shown in the figure, with increasing oxygen ratio, the peak intensity of N–H bonding was decreased, therefore, the unstable film properties shown with the oxygen ratio less than $R=0.3$ appears to be related to the unstable N–H bonding (binding energy: 3.4 eV) remaining in the film [21–23]. Also, the addition of NH_3 appears not to help in the formation of Si–N bonds in the film. The increase of oxygen ratio also decreased the peaks related to Si–N, Si–CH_2–Si, Si–$(CH_3)_x$, and Si–H while increasing the peak related to Si–O, therefore, the film was changed to oxygen-rich SiO_xN_y with less impurities such as carbon and hydrogen.

Using the SiO_xN_y film deposited with $R=0.5$ and 5 sccm of HMDS, the material properties as the diffusion barrier to water permeation was investigated and the results are shown in Fig. 5. On the 200 μm thick PES, the SiO_xN_y was deposited with the structure of PES (200 μm)/parylene (100 nm)/SiO_xN_y (60 nm)/parylene (100 nm). As references, the WVTR of 200 μm thick PES and PES (200 μm)/parylene (800 nm) were also inserted [1]. The test environment was 100% RH, 37.8 °C with N_2 flow rate of 6.4 sccm. As shown in the figure, the WVTR of 200 μm thick PES was 54.10 gm/(m^2 day) and that of PES (200 μm)/parylene (800 nm) was 40.4 gm/(m^2 day), therefore, PES and parylene did not show the property as the water diffusion barrier. However, as shown in the figure, by adding 60 nm thick SiO_xN_y, the significant improvement of WVTR of 0.3 gm/(m^2 day) could be obtained. Currently, the obtained WVTR with 60 nm thick SiO_xN_y is not enough for the application to OTFT devices because it requires WVTR of $\sim 10^{-2}$ gm/(m^2 day). However, it is believed that by using a thicker SiO_xN_y or by using a multiple layer SiO_xN_y, the WVTR required for OTFT and even for OLED could be obtained.

4. Conclusions

SiO_xN_y was deposited using PECVD with HMDS/O_2/Ar/NH_3 as a function of the ratio of $O_2/(O_2+NH_3)$ at a low substrate temperature (40 °C) and its properties as the diffusion barrier to water permeation were investigated. The characteristic of deposited SiO_xN_y was changed with oxygen percentage in the gas mixture. With oxygen ratio lower than 0.3, the film was not stable and soft due to the impurities in the film, however, with increasing oxygen percentage, the film became more stable and harder in addition to higher transparency. Also, with increasing oxygen percentage in the gas mixture, the film became more oxygen-rich SiO_xN_y by replacing Si–N bondings to Si–O bondings in addition to replacing Si–H and Si–C to Si–O. When WVTR was measured for the structure of PES (200 μm)/parylene (100 nm)/SiO_xN_y (60 nm)/parylene (100 nm) with SiO_xN_y deposited with $R=0.5$, the WVTR of 0.3 gm/(m^2 day) could be obtained.

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