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Properties of SiO_xN_y thin film deposited by low temperature plasma enhanced chemical vapor deposition using TEOS–NH_3–O_2–N_2 gas mixtures

J.H. Lee*, C.H. Jeong, J.T. Lim, N.G. Jo, S.J. Kyung, G.Y. Yeom

Department of Materials Science and Engineering, Sungkyunkwan University, 300, Chunchun-Dong, Jangan-Gu, Suwon, 440746, South Korea

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Abstract

In this study, a SiO_xN_y thin film was deposited on plastic substrates using tetraethylorthosilicate (TEOS)/O_2/N_2/NH_3 gas mixtures at a low temperature using the plasma enhanced chemical vapor deposition (PECVD) driven by an inductively coupled plasma (ICP) with a capacitively coupled plasma (CCP) for biasing. Also, the effects of TEOS, N_2, and NH_3 gas flow rates on the properties of the deposited film were investigated. A transparent and impurity free SiO_xN_y film having 60 nm/min of deposition rate could be obtained at the gas mixture of 15 sccm TEOS in N_2, 10 sccm O_2, 75 sccm of N_2, and 20 sccm of NH_3 for 300 W of 13.56 MHz rf power and -150 V of dc bias voltage. When a multilayer film composed of total nine layers (parylene (800 nm)/SiO_xN_y (60 nm)/parylene (280 nm)/SiO_xN_y (60 nm)/...) was deposited on 200 μm-thick polyethersulfone (PES) using the optimized SiO_xN_y, the water vapor transmission rate (WVTR) of 0.0235 g/(m^2 day) could be obtained.

Keywords: PECVD; TEOS; Siliconoxynitride; Passivation; WVTR

1. Introduction

Recently, organic-based display devices such as organic thin film transistors (OTFTs) and organic light emitting diodes (OLEDs) are widely investigated due to the flexibility of the devices, light weight, etc. Especially, OLEDs have shown many advantages such as low driving voltage, high luminance, wide viewing angle, quick response time, etc. [1–3]. Progress in this field has led to the realization of OLEDs with power efficiency and color tunability that are adequate for commercialization. However, one of the major problems of these organic-based devices is short device lifetime and one of the reasons is caused by the permeation of H_2O and O_2 during the exposure to the air.

To prevent the permeation of H_2O and O_2 to the devices, the encapsulation of the devices such as metal encapsulation and glass encapsulation are currently used for OLED devices, however, thin film passivation instead of the encapsulation on these devices are preferred for the lighter weight, wider viewing angle, flexibility, etc. Therefore, various permeation barrier materials and various deposition methods for these materials are intensively investigated for the passivation of the next generation flexible flat panel display (FPD) devices such as OTFTs and OLEDs [4–6].

SiO_xN_y film is one of the widely used dielectric materials used in the solid state electronic and optoelectronic devices as insulators, waveguides, defect passivation etc. [7–9]. SiO_xN_y film is currently deposited by various methods such as physical vapor deposition (PVD), low pressure chemical vapor deposition (LPCVD), plasma enhanced CVD (PECVD), etc. Among these deposition methods, PECVD is a well characterized technique, which allows uniform and conformal deposition of thin films over very large areas at a low temperature [10–12].

In this study, using tetraethylorthosilicate (TEOS)/NH_3/O_2/N_2 gas mixtures, SiO_xN_y thin films were deposited on plastic substrates at a low temperature using a PECVD method and its properties were investigated. TEOS was used

* Corresponding author.
E-mail addresses: omega1234@skku.edu (J.H. Lee), gyyeom@skku.edu (G.Y. Yeom).

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as the precursor of Si because it shows a good step coverage after the deposition and it is safe, easy to handle as a liquid form, and chemically stable compared to other silicon precursors such as SiH_4, SiH_xCl_y, etc. [10,11] Also, by forming multiple layers of SiO_xN_y/parylene, the water permeation properties of the deposited SiO_xN_y films were also investigated.

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 ICP source made of a 3-turn copper coil and operated at 300 W 13.56 MHz was used for the high dissociation of gas molecules. The substrate was maintained at lower than 45 °C using a chiller and biased at −150 V using a separate 13.56 MHz rf power. Gas mixtures were supplied to the reactor using a gas ring located on the top of the chamber. The gas mixtures composed of tetraethylorthosilicate (TEOS)/NH_3/O_2/N_2 were used to deposit SiO_xN_y. In this gas mixture, TEOS was delivered to the chamber by heating the TEOS liquid source at 50 °C using a water bath and by carrying it by N_2 through stainless tubing heated to 80 °C. The flow rates of TEOS (0~60 sccm), NH_3 (0~60 sccm), and N_2 (0~100 sccm) were varied for the optimization of the SiO_xN_y film. O_2 flow rate was maintained at 10 sccm.

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 an 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, in addition to the SiO_xN_y, a parylene film known to have excellent chemical stability, optical transmittance, and step coverage [13,14] was deposited on the PES alternatively to form a multilayer film composed of inorganic SiO_xN_y films and organic parylene films. The parylene film was deposited by a parylene coater (SCS Inc., PDS 2010 LABCOTER). The water vapor transmission rate (WVTR) was measured using a WVTR measurement system (MOCON Inc., PERMATRAN-W Model3/33).

3. Results and discussion

Fig. 2 shows the SiO_xN_y deposition rate as a function of gas flow rates such as TEOS, NH_3, and N_2 for 10 sccm of O_2, 300 W of ICP power, and −150 V of dc bias voltage. When one of the gas flow rates was varied, the other gas

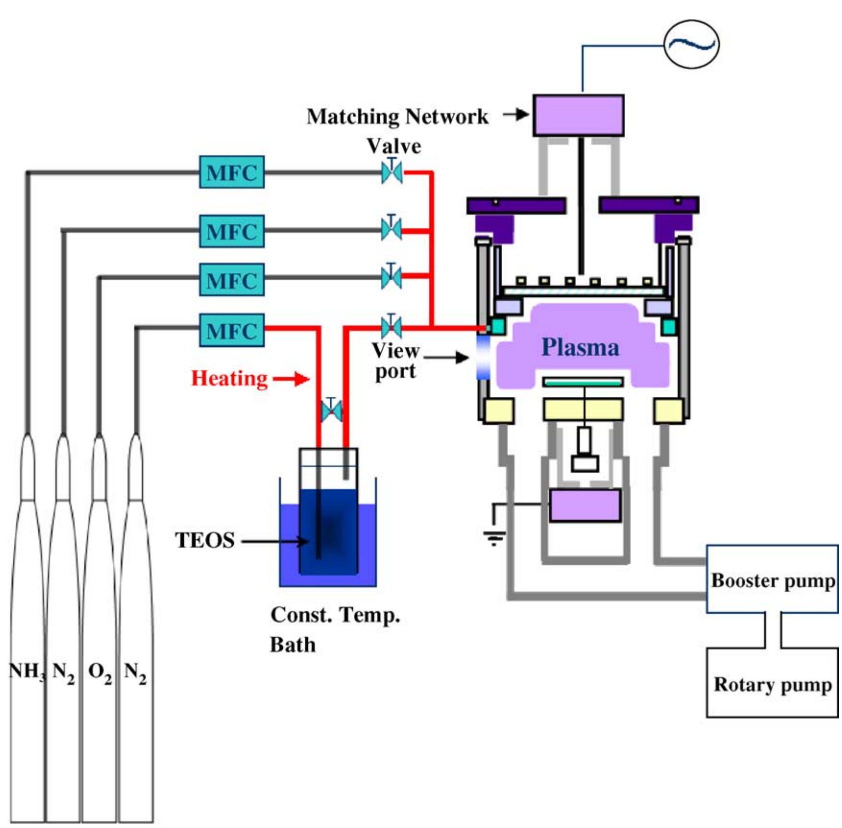

Fig. 1. Schematic illustration of an ICP-type PECVD apparatus with a bubbling system of TEOS used in this study.

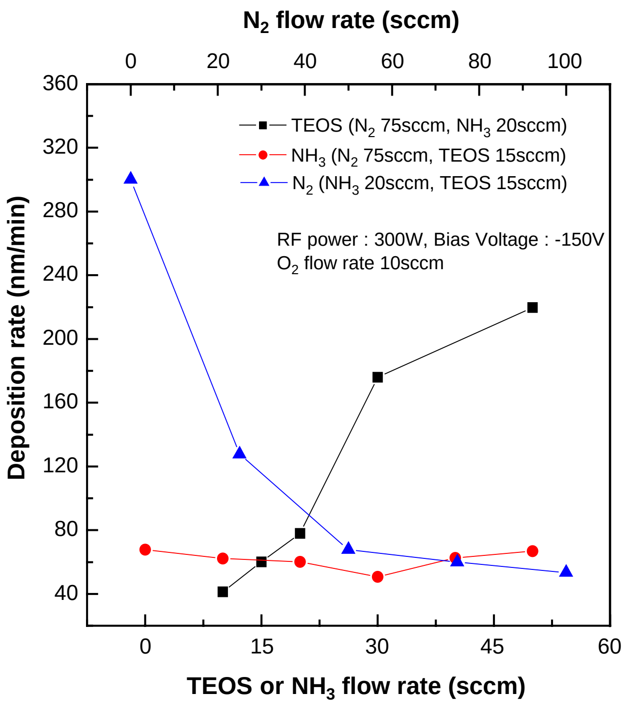

Fig. 2. Deposition rate of SiO_xN_y films as a function of TEOS flow rate; NH_3 flow rate; and N_2 flow rate at 300 W of the rf power and −150 V dc bias voltage.

flow rates of TEOS, NH_3, and N_2 were maintained at 15, 20, and 75 sccm, respectively. With these gas flow rates, the operating pressure was in the range from 96 to 135 mTorr. As shown in the figure, the increase of TEOS gas flow rate from 8 to 50 sccm increased the deposition rate of SiO_xN_y from 41 to 219 nm/min. However, in the case of N_2 and NH_3, the increase of N_2 flow rate from 0 to 100 sccm decreased the SiO_xN_y deposition rate significantly from 300 to 53 nm/min while the increase of NH_3 did not change the deposition rate significantly and showed about 63 nm/min. The increase of SiO_xN_y deposition rate with the increase of TEOS gas flow rate is related to the increased percentage of the silicon precursor in the gas mixture for the formation of SiO_xN_y film, however, with the increase of TEOS flow rate, possibly due to the increase of incompletely dissociated TEOS deposited on the substrate, the deposited SiO_xN_y film became less transparent, softer and more easily peeled-off. Therefore, the TEOS flow rate was maintained at 15 sccm for other experiments. In the case of N_2, with increasing the N_2 flow rates, the deposited SiO_xN_y showed more transparent and hard film characteristics (not shown) even though the increase of N_2 addition decreased the SiO_xN_y deposition rate. In the case of NH_3, when more than 20 sccm of NH_3 was added, the film became less transparent and some kind of stain was observed on the surface of the deposited film.

To understand the effect of N_2 and NH_3 on the deposited SiO_xN_y, the characteristics of SiO_xN_y deposited as a function of N_2 and NH_3 were investigated using XPS and FTIR. Table 1 shows the atomic composition of SiO_xN_y thin film deposited as functions of N_2 and NH_3 flow rates using XPS. The SiO_xN_y deposition conditions are the same as those in Fig. 2. As shown in the table, when N_2 flow rate was increased from 0 to 75 sccm, the carbon percentage in the SiO_xN_y film was decreased from 12.2% to 0.4% and the oxygen percentage in the film was increased from 51.1% to 62.0%. The observed increase of optical transmittance with increasing N_2, therefore, appears related to the decrease of carbon percentage and the increase of oxygen percentage in the film. The decrease of carbon with increasing N_2 appears related to the removal of carbon in the growing film possibly by the formation of CN from the growing film and replacing the removed carbon site by oxygen in the gas mixture (TEOS + 2O → C_2H_5O–SiO + products) [15]. Nitrogen itself appeared not get involved in the growing film even though nitrogen was added to 75 sccm (more than 62% of the gas mixture). The nitrogen of about a few percent observed in the SiO_xN_y film was originated not from the N_2 but from the NH_3 added in the gas mixture. It can be seen clearly from the XPS data when the addition of NH_3 was varied from 0 to 50 sccm. When no NH_3 was added in the gas mixture, no nitrogen was observed in the film. Also, as shown in the Table 1, the nitrogen content observed in the film was about 1.5% after a small gas flow rate of NH_3 was added to the gas mixture, however, the increased flow rate of NH_3 did not increase the nitrogen percentage in the film. Therefore, the addition of NH_3 to the gas mixture added the nitrogen in the film, however, it did not significantly changed the composition of the film with NH_3 flow rate. The decrease of SiO_xN_y deposition rate with the increase of N_2 shown in Fig. 2, therefore, appears partially related to the decreased percentage of TEOS in the gas mixture with increasing N_2 flow rate without involving in the film growth. Also, the increased sputter etching of SiO_xN_y by the increased nitrogen ions (N_2^+) in the plasma and the difficulty in forming dissociated nitrogen atoms in N_2/TEOS/O_2/NH_3 plasma ($N_2 \rightarrow 2N$, $E = 9.8$ eV) [16] might be also related to the decrease of SiO_xN_y deposition rate with increasing N_2 in the plasma. Also, the insignificant change of SiO_xN_y deposition rate with increasing NH_3 appears

Table 1
Atomic percentage of SiO_xN_y thin films deposited at different N_2 gas rates and NH_3 gas flow rates measured by XPS

N_2 flow rate (sccm)	0	25	50		75	
Si2p (%)	34.5	35.9	36.9		36.1	
C1s (%)	12.21	7.28	1.08		0.41	
N1s (%)	2.24	3.03	2.12		1.51	
O1s (%)	51.1	53.7	60.0		62.0	
NH_3 flow rate (sccm)	0	10	20	30	40	50
Si2p (%)	37.6	36.7	36.1	36.1	37.3	37.0
C1s (%)	0.33	0.4	0.4	0.4	0.2	0.5
N1s (%)	0	1.6	1.5	1.1	1.4	1.4
O1s (%)	62.0	61.4	62.0	62.3	61.1	61.1

related to the negligible participation of nitrogen in NH_3 in the film except for a small percentage.

Fig. 3(a) and (b) show the FTIR spectra of the SiO_xN_y flms grown as a function of N_2 flow rate and NH_3 flow rate, respectively. The deposition conditions of the SiO_xN_y films were the same as those in Fig. 2. The thickness of the deposited SiO_xN_y films was about 300 nm. As shown in the figure, the absorption peaks related to Si–O bonding were observed at 439.74, 800.41, 1064.65, and 1189.3 cm^{-1} [17,18] and a small absorption peak corresponding to Si–N bonding was observed at 952.78 cm^{-1} [17,18]. Therefore, from the data, the formation of SiO_2-like films with a small percentage of Si–N bondings could be identified. In addition, in the FTIR data, an absorption peak related to N–H bonding was observed at 3328.91 cm^{-1} [17,18] when N_2 flow rate was low or when the NH_3 flow rate was high in the TEOS/N_2/O_2/NH_3 gas mixture. The formation of N–H bonding with the increase of NH_3 appears to show the inefficient dissociation of NH_3 ($NH_3 \rightarrow NH_2 + H$, $NH_3 \rightarrow NH + H_2$) [19]. Less transparency and stain-like features obtained with the NH_3 gas flow rate higher than 20 sccm, therefore, appears related to the formation unstable N–H bonding (binding energy: 3.5 eV) in the film [20]. The increase of N_2 flow rate appears to remove the hydrogen in N–H involved in the film.

Even though the addition of N_2 did not increase the nitrogen content in the growing SiO_xN_y film, some Si–N bondings were formed by small addition of NH_3 and the

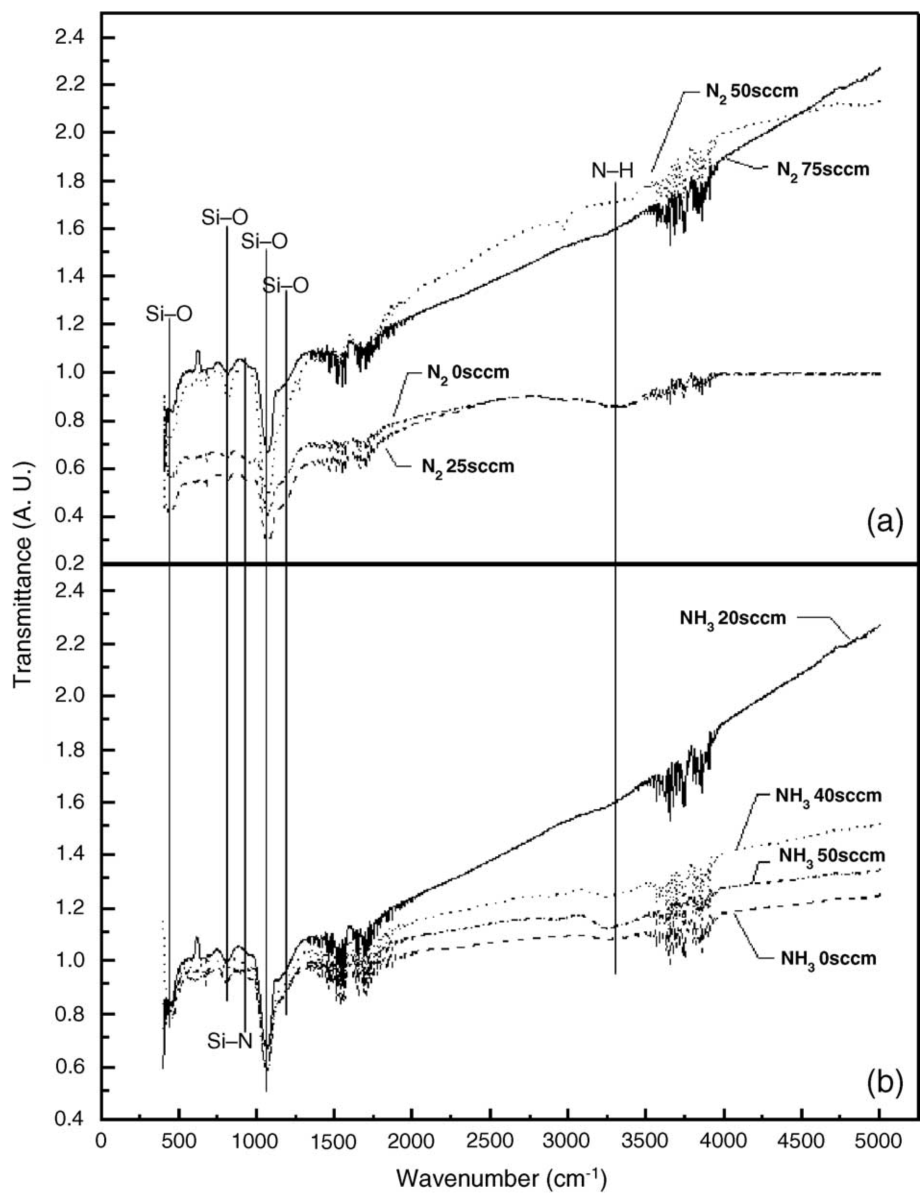

Fig. 3. FT-IR spectra of the SiO_xN_y deposited under different (a) N_2 gas flow rate and (b) NH_3 gas flow rate by the PECVD (process condition: TEOS 15 sccm, O_2 flow rate 10 sccm, rf power 300 W, and dc bias voltage −150 V. Also, when NH_3 was varied, N_2 flow rate was 75 sccm and, when NH_3 flow rate was varied, NH_3 flow rate was 20 sccm).

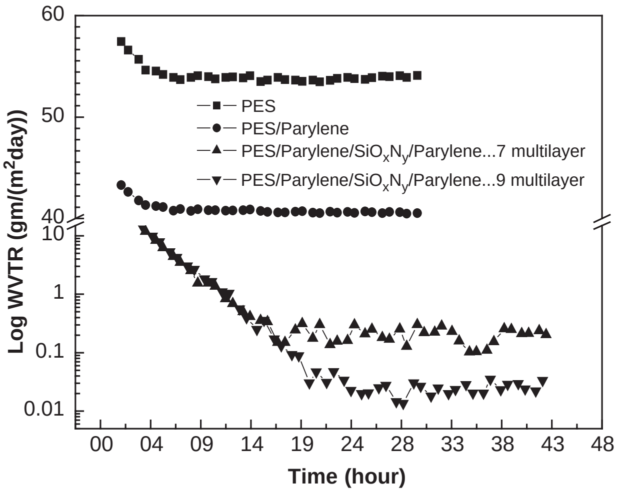

Fig. 4. WVTR of multilayer thin films composed of parylene (800 nm)/ SiO_xN_y (60nm)/parylene (280 nm)/SiO_xN_y (600 nm)/. . .) on 200 μm-thick PES.

impurities such as carbon and hydrogen in the film could be removed by the addition of N_2 in the gas mixture. The optimized gas mixture obtained in our experiment by considering the impurity percentage of the film, optical transmittance, and deposition rate was TEOS 15 sccm, O_2 10 sccm, N_2 75 sccm, and NH_3 20 sccm, and, at this condition, a transparent film with deposition rate of about 60 nm/min could be obtained. Using this optimized SiO_xN_y, the water permeation property was investigated by forming multilayers composed of parylene and SiO_xN_y on 200 μm-thick PES. Fig. 4 shows the WVTR of multilayer films composed of parylene (800 nm)/SiO_xN_y (60 nm)/parylene (280 nm)/SiO_xN_y (60 nm)/. . . on the PES. Total layers in the multilayer films were seven layers and nine layers. The measurement condition was 100% relative humidity (RH), 37.8 °C, and 10.5 sccm of N_2 flow rate. As shown in the figure, the multilayer film composed of seven layers showed 0.202 g/(m^2 day) of WVTR and the film composed of nine layers showed 0.0235 g/(m^2 day). The WVTR of 200 μm-thick PES itself was 54.10 g/(m^2 day) and that of PES (200 μm)/parylene (800 nm) was 40.4 g/(m^2 day). The WVTR of the multilayer films used in the experiment was not as low as ~10^{-6} g/(m^2 day) required as the permeation barrier for the OLEDs, however, it was close to the WVTR (~10^{-2} g/(m^2 day)) required for the OTFTs. Even though the pinholes were not detected by an optical microscope, it appears to be the origin of the high WVTR of the multilayer film composed of parylene and SiO_xN_y investigated in this study. The exact reason is under investigation.

4. Conclusions

In this study, SiO_xN_y film was deposited by a low temperature ICP-type PECVD (lower than 45 °C) on plastic substrates as a function of, TEOS, N_2, and NH_3 gas flow rate in the TEOS/O_2/N_2/NH_3 gas mixtures while keeping rf power to the ICP source at 300 W and dc bias voltage to the substrate at − 150 V.

The deposited SiO_xN_y films were SiO_2-like films with a small percentage of Si–N bondings in the film. During the deposition, the increase of N_2 in the gas mixture did not add any nitrogen in the growing film and decreased the deposition rate of SiO_xN_y, however, it removed carbon and hydrogen in the film, therefore, the optical transmittance was improved. The addition of small NH_3 flow rate added nitrogen in the film, however, high NH_3 percentages in the gas mixtue increased N–H bondings in the film without increasing nitrogen percentage in the film. A transparent and impurity free SiO_xN_y film having 60 nm/min of deposition rate could be obtained at the gas mixture of 15 sccm TEOS, 10 sccm O_2, 75 sccm of N_2, and 20 sccm NH_3. When the water permeation property of the deposited SiO_xN_y film was investigated using mutilayer films composed of parylene and SiO_xN_y, the WVTR of 0.0235 g/(m^2 day) could be obtained when the multilayer film composed of total nine layers (parylene (800 nm)/SiO_xN_y (60 nm)/parylene (280 nm)/SiO_xN_y (60 nm)/. . .) were deposited on the 200 μm-thick PES. Even though it satisfies the WVTR required for OTFTs (~10^{-2} g/(m^2 day)), it needs more investigation on the leakage source of the SiO_xN_y films to satisfy the WVTR required for OLEDs (~10^{-6} g/(m^2 day)).

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