Properties of SiO$_x$N$_y$ thin film deposited by low temperature plasma enhanced chemical vapor deposition using TEOS–NH$_3$–O$_2$–N$_2$ gas mixtures


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

Available online 13 April 2005

Abstract

In this study, a SiO$_x$N$_y$ 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$_x$N$_y$ 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$_x$N$_y$ (60 nm)/parylene (280 nm)/SiO$_x$N$_y$ (60 nm)/… was deposited on 200 μm-thick polyethersulfone (PES) using the optimized SiO$_x$N$_y$, the water vapor transmission rate (WVTR) of 0.0235 g/(m$^2$ day) could be obtained.

© 2005 Elsevier B.V. All rights reserved.

Keywords: PECVD; TEOS; Silicoxynitride; 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$_2$O and O$_2$ during the exposure to the air.

To prevent the permeation of H$_2$O 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$_x$N$_y$ 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$_x$N$_y$ 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$_x$N$_y$ thin films were deposited on plastic substrates at a low temperature using a PECVD method and its properties were investigated. TEOS was used...
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 SiH₄, SiHₓClₙ, etc. [10,11] Also, by forming multiple layers of SiOₓNᵧ/parylene, the water permeation properties of the deposited SiOₓNᵧ films were also investigated.

2. Experimental

Fig. 1 shows the schematic diagram of the PECVD reactor used in this experiment for the deposition of SiOₓNᵧ 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)/NH₃/O₂/N₂ were used to deposit SiOₓNᵧ. 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 N₂ through stainless tubing heated to 80 °C. The flow rates of TEOS (0~60 sccm), NH₃ (0~60 sccm), and N₂ (0~100 sccm) were varied for the optimization of the SiOₓNᵧ film. O₂ flow rate was maintained at 10 sccm.

SiOₓNᵧ 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 profilerometer (Tencor Inc. Alpha-step 500). The chemical compositions and binding states of the deposited SiOₓNᵧ 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 SiOₓNᵧ, 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 SiOₓNᵧ 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 SiOₓNᵧ deposition rate as a function of gas flow rates such as TEOS, NH₃, and N₂ for 10 sccm of O₂, 300 W of ICP power, and −150 V of dc bias voltage. When one of the gas flow rates was varied, the other gas
flow rates of TEOS, NH₃, and N₂ 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 SiOₓNy from 41 to 219 nm/min. However, in the case of N₂ and NH₃, the increase of N₂ flow rate from 0 to 100 sccm decreased the SiOₓNy deposition rate significantly from 300 to 53 nm/min while the increase of NH₃ did not change the deposition rate significantly and showed about 63 nm/min. The increase of SiOₓNy deposition rate with the increase of TEOS gas flow rate is related to the increase of the silicon precursor in the gas mixture for the formation of SiOₓNy film, however, with the increase of TEOS flow rate, possibly due to the increase of incompletely dissociated TEOS deposited on the substrate, the deposited SiOₓNy 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 N₂, with increasing the N₂ flow rates, the deposited SiOₓNy showed more transparent and hard film characteristics (not shown) even though the increase of N₂ addition decreased the SiOₓNy deposition rate. In the case of NH₃, when more than 20 sccm of NH₃ 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 N₂ and NH₃ on the deposited SiOₓNy, the characteristics of SiOₓNy deposited as a function of N₂ and NH₃ were investigated using XPS and FTIR. Table 1 shows the atomic composition of SiOₓNy thin film deposited as functions of N₂ and NH₃ flow rates using XPS. The SiOₓNy deposition conditions are the same as those in Fig. 2. As shown in the table, when N₂ flow rate was increased from 0 to 75 sccm, the carbon percentage in the SiOₓNy 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 N₂, therefore, appears related to the decrease of carbon percentage and the increase of oxygen percentage in the film. The decrease of carbon with increasing N₂ 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→C₂H₅O–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 SiOₓNy film was originated not from the N₂ but from the NH₃ added in the gas mixture. It can be seen clearly from the XPS data when the addition of NH₃ was varied from 0 to 50 sccm. When no NH₃ 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 NH₃ was added to the gas mixture, however, the increased flow rate of NH₃ did not increase the nitrogen percentage in the film. Therefore, the addition of NH₃ to the gas mixture added the nitrogen in the film, however, it did not significantly changed the composition of the film with NH₃ flow rate. The decrease of SiOₓNy deposition rate with the increase of N₂ shown in Fig. 2, therefore, appears partially related to the decreased percentage of TEOS in the gas mixture with increasing N₂ flow rate without involving in the film growth. Also, the increased sputter etching of SiOₓNy by the increased nitrogen ions (N₂⁺) in the plasma and the difficulty in forming dissociated nitrogen atoms in N₂/TEOS/O₂/NH₃ plasma (N₂→2N, E=9.8 eV) [16] might be also related to the decrease of SiOₓNy deposition rate with increasing N₂ in the plasma. Also, the insignificant change of SiOₓNy deposition rate with increasing NH₃ appears.

![Graph](image_url)

**Fig. 2.** Deposition rate of SiOₓNy films as a function of TEOS flow rate; NH₃ flow rate; and N₂ flow rate at 300 W of the rf power and −150 V dc bias voltage.

**Table 1**

<table>
<thead>
<tr>
<th>N₂ flow rate (sccm)</th>
<th>0</th>
<th>25</th>
<th>50</th>
<th>75</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si2p (%)</td>
<td>34.5</td>
<td>35.9</td>
<td>36.9</td>
<td>36.1</td>
</tr>
<tr>
<td>Cls (%)</td>
<td>12.21</td>
<td>7.28</td>
<td>1.08</td>
<td>0.41</td>
</tr>
<tr>
<td>Nls (%)</td>
<td>2.24</td>
<td>3.03</td>
<td>2.12</td>
<td>1.51</td>
</tr>
<tr>
<td>Ols (%)</td>
<td>51.1</td>
<td>53.7</td>
<td>60.0</td>
<td>62.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>NH₃ flow rate (sccm)</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si2p (%)</td>
<td>37.6</td>
<td>36.7</td>
<td>36.1</td>
<td>36.1</td>
<td>37.3</td>
<td>37.0</td>
</tr>
<tr>
<td>Cls (%)</td>
<td>0.33</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.2</td>
<td>0.5</td>
</tr>
<tr>
<td>Nls (%)</td>
<td>0.0</td>
<td>1.6</td>
<td>1.5</td>
<td>1.1</td>
<td>1.4</td>
<td>1.4</td>
</tr>
<tr>
<td>Ols (%)</td>
<td>62.0</td>
<td>61.4</td>
<td>62.0</td>
<td>62.3</td>
<td>61.1</td>
<td>61.1</td>
</tr>
</tbody>
</table>
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$_x$N$_y$ films grown as a function of N$_2$ flow rate and NH$_3$ flow rate, respectively. The deposition conditions of the SiO$_x$N$_y$ films were the same as those in Fig. 2. The thickness of the deposited SiO$_x$N$_y$ 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$_3$ → NH$_2$ + H, NH$_3$ → 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$_x$N$_y$ film, some Si–N bondings were formed by small addition of NH$_3$ and the
impurities such as carbon and hydrogen in the film could be removed by the addition of N2 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, O2 10 sccm, N2 75 sccm, and NH3 20 sccm. And, at this condition, a transparent film with deposition rate of about 60 nm/min could be obtained. Using this optimized SiOxNy, the water permeation property was investigated by forming multilayers composed of parylene and SiOxNy on 200 μm-thick PES. Fig. 4 shows the WVTR of multilayer thin films composed of parylene (800 nm)/SiOxNy (60 nm)/parylene (280 nm)/SiOxNy (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 N2 flow rate. As shown in the figure, the multilayer film composed of seven layers showed 0.202 g/(m² day) of WVTR and the film composed of nine layers showed 0.0235 g/(m² day). The WVTR of 200 μm-thick PES itself was 54.10 g/(m² day) and that of PES (200 μm)/parylene (800 nm) was 40.4 g/(m² day). The WVTR of the multilayer films used in the experiment was not as low as ~10⁻⁶ g/(m² day) required as the permeation barrier for the OLEDs, however, it was close to the WVTR (~10⁻² g/(m² 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 SiOxNy investigated in this study. The exact reason is under investigation.

4. Conclusions

In this study, SiOxNy film was deposited by a low temperature ICP-type PECVD (lower than 45 °C) on plastic substrates as a function of, TEOS, N2, and NH3 gas flow rate in the TEOS/O2/N2/NH3 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 SiOxNy films were SiO2-like films with a small percentage of Si–N bondings in the film. During the deposition, the increase of N2 in the gas mixture did not add any nitrogen in the growing film and decreased the deposition rate of SiOxNy, however, it removed carbon and hydrogen in the film, therefore, the optical transmittance was improved. The addition of small NH3 flow rate added nitrogen in the film, however, high NH3 percentages in the gas mixtue increased N–H bondings in the film without increasing nitrogen percentage in the film. A transparent and impurity free SiOxNy film having 60 nm/min of deposition rate could be obtained at the gas mixture of 15 sccm TEOS, 10 sccm O2, 75 sccm of N2, and 20 sccm NH3. When the water permeation property of the deposited SiOxNy film was investigated using mutilayer films composed of parylene and SiOxNy, the WVTR of 0.0235 g/(m² day) could be obtained when the multilayer film composed of total nine layers (parylene (800 nm)/SiOxNy (60 nm)/parylene (280 nm)/SiOxNy (60 nm)/... were deposited on the 200 μm-thick PES. Even though it satisfies the WVTR required for OTFTs (~10⁻² g/(m² day)), it needs more investigation on the leakage source of the SiOxNy films to satisfy the WVTR required for OLEDs (~10⁻⁶ g/(m² day)).

Acknowledgements

This work was supported by the Ministry of Commerce, Industry and Energy, the National Research Laboratory Program (NRL) by the Korea Ministry of Science and Technology. We would like to thank ATMI (Advanced Technology Materials, Inc.) for supplying the TEOS source.

References