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Plasma-Enhanced Chemical Vapor Deposition of SiO_2 Thin Films at Atmospheric Pressure by Using HMDS/Ar/O_2

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SiO_2-like thin films were deposited at low temperature (<50 °C) by using atmospheric-pressure plasma-enhanced chemical vapor deposition (AP-PECVD) with a pin-to-plate type dielectric barrier discharge (DBD) and a gas mixture containing hexamethyldisilazane (HMDS)/Ar/O_2. The film's characteristics were investigated as a function of the HMDS flow rate. Increasing the HMDS flow rate from 100 sccm to 500 sccm increased the deposition rate almost linearly from 46.4 nm/min to 141.1 nm/min. However, increasing the HMDS flow rate increased impurities such as C and H and the surface roughness of the deposited film. Fourier transform infrared measurement showed an increase of -OH and -$(CH_3)_x$ (x = 1, 2 or 3) in the film with increasing HMDS flow rate. The increased surface roughness and impurities in the deposited film are believed to be related to incompletely dissociated HMDS at higher HMDS flow rates. By optimizing the oxygen flow rate and the HMDS flow rate, we believe that a SiO_2 thin film with low impurity and low surface roughnesses can be obtained. In this experiment, with the HMDS flow rate in the range of 100 ~ 200 sccm, SiO_2-like thin films having low surface roughness and low impurities (<3.7 % C) could be obtained.

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I. INTRODUCTION

These days, flexible displays utilizing flexible polymer substrates are actively being investigated as the most promising next generation display devices [1]. However, most flexible substrates, such as plastic substrates, are vulnerable to the environment factors such as oxygen, moisture, scratches, *etc.*, due to the softness of the material and due to the diffusion of vapor through the substrate film during the exposure to atmosphere. To protect the flexible displays from the atmosphere, a thin-film diffusion barrier composed of a single inorganic layer or a multilayer (a multiple-layer thin film composed of organic layer and inorganic layers) should be deposited both on the flexible substrate and on the surface of the display device deposited on the flexible substrate.

Among the various inorganic thin films, the SiO_2 thin film is one of the most investigated materials for many applications, such as solid state electronics [2], optoelectronic devices [3], *etc.*, as well as thin film diffusion barriers. For the deposition of SiO_2 thin films, chemical vapor deposition (CVD) is a quite suitable method for the production of high-quality thin films that can be applied to a wide variety of electronic applications [4,5]. In particular, plasma-enhanced CVD (PECVD) has been used for the deposition of SiO_2 thin films at a low temperature for thermally sensitive materials [25]. However, a drawback of this technique is that it is carried out inside a vacuum chamber, which is costly and requires significant maintenance [6]. Furthermore, it is difficult to accommodate the in-line processing, that may be required for next generation flexible display processing. In an effort to eliminate some of these drawbacks, alternative deposition methods are under development, including atmospheric-pressure PECVD (AP-PECVD) [7].

One of the most investigated plasma sources generated at atmospheric pressure is the dielectric barrier discharge (DBD) composed of two parallel blank electrodes covered by dielectrics. By using the DBD, a uniform and large-area glow discharge can be generated. In this study, a modified DBD composed of a multi-pin power electrode, instead of blank power electrode, was used as the plasma source to generate a higher plasma density. Also to deposit SiO_2 thin film, we used a gas mixture composed

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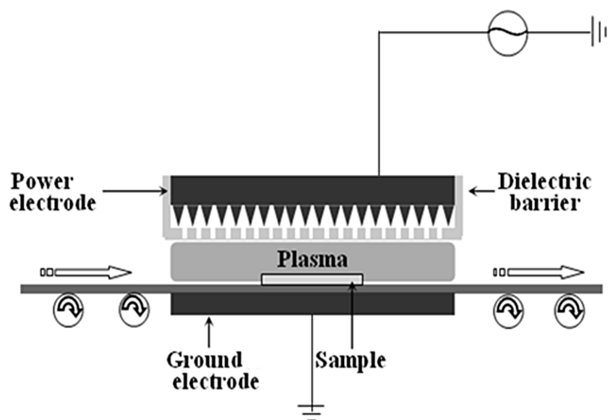

Fig. 1. Schematic diagram of the AP-PECVD in-line system (pin-to-plate DBD-type).

of hexamethyldisilazane (HMDS, 99.9 %)/O_2/Ar. Then, we investigated the effect of the HMDS flow rate on the characteristics of SiO_2 deposited at a low temperature to study the possibility of depositing a SiO_2 thin film on a flexible substrate by using AP-PECVD.

II. EXPERIMENTS

Figure 1 shows the AP-PECVD system used to deposit the SiO_2 film. The plasma source consisted of two parallel electrodes (198 mm length × 105 mm width) composed of a power electrode and a ground electrode. These electrodes were covered with an insulating ceramic plate and were separated by approximately 8 mm. The power electrode was made of a multi-pin-type electrode, instead of a blank electrode, as shown in the figure (pin-to-plate DBD) to operate at a low breakdown voltage and to have higher plasma densities due to the higher electric field on the multi-pin at the same applied voltage, as shown in a previous study [8].

Atmospheric pressure plasma discharges were generated by applying a 14 kV AC voltage at a frequency of 25 kHz to the multi-pin electrode. The substrate temperature was maintained at <50 °C by using a chiller. The process gas was fed into the system through the shower slits in the ceramic material of the power electrode. The substrate was fed to the AP-PECVD system at 0.3 m/min through an in-line feeder. HMDS (Sigma-Aldrich Co., purity 99.9 %, $Si_2NH(CH_3)_6$) was used as the Si precursor because it is relatively safe and non-corrosive and become it has been widely used in the integrated circuit industry as a photoresist adhesion promoting agent [9]. Also, SiO_2 thin films produced with HMDS are known to contain significantly less OH and to hard lower porosity than films grown using other silicon precursors, such as tetramethylcyclotetrasilocane (TMCTS), tetraethoxysilane (TEOS), tetramethyldisioxane (TMDSO), *etc.* [10]. HMDS was fed into the system by

Table 1. Process parameters used in the deposition of SiO_2 in this experiment.

Substrate	Si wafer, Glass
Gas chemistry	HMDS/Ar + Ar + O_2
Deposition temperature	<50 °C
AC voltage	14 kV
Bubbler temperature	50 °C
Line speed	0.3 m/min
Flow rate of Ar flow in HMDS	100 ∼ 500 sccm
Flow rate of Ar	10 slm
Flow rate of O_2	30 slm

bubbling Ar through a HMDS liquid reservoir kept at 50 °C.

Silicon wafers and sodalime glass were used as the substrates and gas mixtures composed of HMDS+O_2+Ar were used to deposit the SiO_2 thin films. The Ar was used as the discharge gas and the O_2 was used for the oxidation of HMDS. In order to investigate the characteristics of the thin film, the HMDS flow rate (bubbles by Ar) was varied from 100 to 500 sccm while the other gas flow rates, such as the flow rates of Ar and O_2, were fixed at 30 slm and 10 slm, respectively. Other detailed operating conditions for depositing the SiO_2 films are summarized in Table 1.

The thickness of the deposited film was measured using a step profilometer (Tencor, Alpha step 500). The composition of the deposited SiO_2 thin film was measured by using X-ray photoelectron spectroscopy (XPS; Thermo Electronics, Multilab ESCA2000). The chemical bonding states of the deposited SiO_2 film were investigated by using Fourier transform infrared spectrometry (FT-IR; Bruker IFS-66/S) and X-ray photoelectron spectroscopy. The surface morphology of the thin films was observed by using a field emission scanning electron microscope (FE-SEM; Hitachi, S-4700).

III. RESULTS AND DISCUSSION

SiO_2 was deposited using the pin-to-plate DBD-type AP-PECVD system as a function of the HMDS flow rate mixed with 10 slm Ar and 30 slm O_2 at a 14 kV AC voltage. To introduce the HMDS to the system, we bubbled the HMDS liquid source by using additional Ar as the carrier gas and the gas line was maintained at 50 °C. Figure 2 shows the SiO_2 deposition rate measured as a function of the HMDS flow rate. As shown in the figure, by increasing the HMDS flow rate from 100 to 500 sccm, the SiO_2 deposition rate was increased from 46.4 ± 3.3 to 141.1 ± 1.4 nm/min; therefore, the deposition rate increased almost linearly with increasing HMDS flow rate in the gas mixture. The increase in the deposition rate with increasing of HMDS flow rate is related to the en-

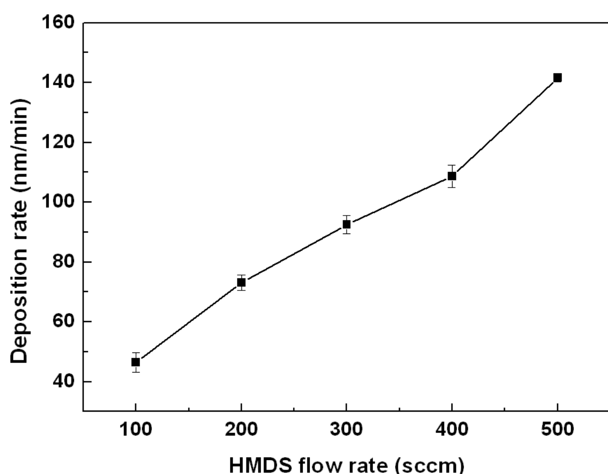

Fig. 2. Deposition rate of SiO_2 films as functions of HMDS flow rate with HMDS/O_2(30 slm) /Ar(10 slm) at an applied voltage of 14 kV (25 kHz).

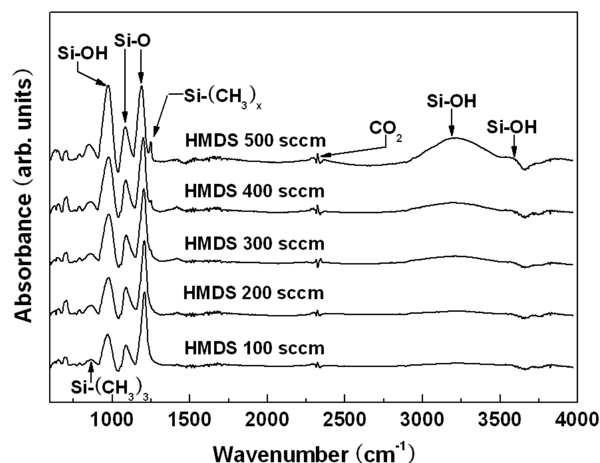

Fig. 3. FT-IR spectra of the SiO_2 deposited by using AP-PECVD at different HMDS flow rates. The deposition conditions are the same as these shown in Figure 2.

hanced reaction of Si from the decomposed HMDS with oxygen in the gas mixture [10]. However, an increase in the HMDS flow rate in the gas mixture not only increases the Si-O bonding in the deposited film but also increases the possibility of depositing organic components, such as those with -CH bonding. Therefore, by using FT-IR, the characteristics of the chemical bonding in the deposited thin films can be investigated.

Figure 3 shows the FT-IR data obtained for a SiO_2 thin film deposited on a Si (p-type <100>) wafer as a function of the HMDS flow rate. The thickness of the deposited SiO_2 film was maintained at 300 nm for all the samples. The absorption peaks related to the Si-OH bond could be observed at wave numbers of 972 – 978 cm^{-1} [7] and 3250 – 3600 cm^{-1} (OH broad band) [11, 12]. In addition, absorption peaks related to the Si-O-Si bond could be observed at 1082 – 1092 $cm^{-1}$and 1188 – 1208 cm^{-1} [13]. Small peaks related to the CO_2 group, Si-$(CH_3)_3$ bonding and Si-$(CH_3)_x$ (x = 1, 2) were also observed at 2321 – 2323 cm^{-1} [14], 850-860 cm^{-1} [15,16] and 1246 – 1260 cm^{-1} [15,16,26], respectively. As shown in the figure, increasing the of HMDS flow rate from 100 to 500 sccm increased the absorption peaks related to Si-OH and Si-$(CH_3)_x$ (x = 1, 2 or 3). The increased Si-OH bonding with increasing of HMDS flow rate appears to be related to the increased possibility of compound formation between hydrogen and incompletely oxidized Si from the decomposed HMDS. However, the increase in bondings related to Si-$(CH_3)_x$ appears to be from the incorporation of CH_x into the film due to the incomplete dissociation of HMDS at increasing of HMDS flow rate. The impurities in the film composed of C and H can be the cause of a less dense film [17]. Especially, an increase in Si-OH bonding in the film is known to increase the absorption of moisture from the air and to decrease the hardness of the deposited film, which it tends to decrease the corrosion resistance and to decrease the chemical and mechanical stability [18,19]. From the figure, the absorption peaks related to -OH and -$(CH_3)_x$ (x = 1, 2 or 3) are considerable for HMDS flow rates higher than 300 sccm; therefore, a film with relatively small impurity could be obtained at HMDS flow rates lower than 200 sccm.

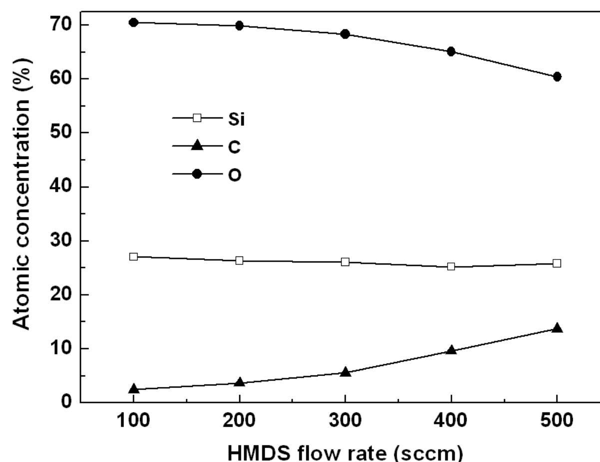

Fig. 4. Atomic composition of thin films deposited at different HMDS flow rates, as measured by XPS. The deposition conditions are the same as these shown in Figure 2.

The composition of the SiO_2 film deposited as a function of HMDS flow rate shown in Figure 2 was investigated using XPS and the result is shown in Figure 4. No hydrogen could be measured due to the XPS detection limit. As shown in the figure, increasing the HMDS flow rate from 100 to 200 sccm decreased the oxygen percentage slightly from 70.5 % to 69.9 % while also decreasing the silicon percentage slightly from 27.1 % to 26.4 %. The carbon percentage increased from 2.5 % to 3.7 %. Therefore, up to 200 sccm of HMDS, the deposited film showed a SiO_2-like film having a low impurity level. However, as shown in the figure, increasing the of HMDS flow rate to higher than 300 sccm, signif-

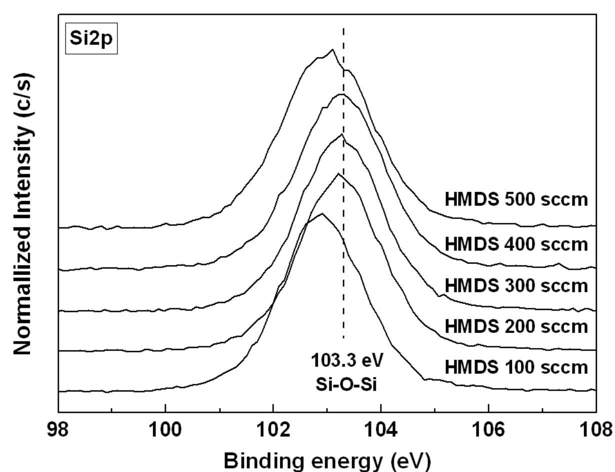

Fig. 5. XPS spectra of Si 2p core levels of the SiO_2 thin films as a function of the HMDS flow rate. The deposition conditions are the same as these shown in Figure 2.

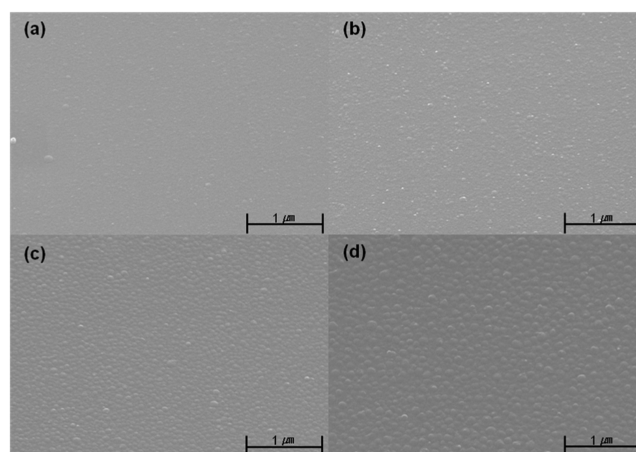

Fig. 6. SEM micrographs of the deposited films as a function of HMDS flow rate: (a) 100 sccm, (b) 200 sccm, (c) 400 sccm and (d) 500 sccm. The deposition conditions are the same as these shown in Figure 2.

icantly increased the carbon percentage in the film to 13.8 % and decreased the oxygen percentage to 60 % at a 500 sccm HMDS flow rate. The increase in the carbon content in the film observed increasing of HMDS flow rate is related to the Si-$(CH_3)_x$ (x = 1, 2 or 3) bondings observed by FT-IR spectrometry. The increase in the carbon impurity and the decrease in oxygen in the film is due to the incompletely dissociated HMDS with increasing HMDS flow rate while keeping the same oxygen flow rate. Especially, for HMDS flow rates higher than 300 sccm, due to the significantly incomplete dissociation of HMDS, the deposited SiO_2 film appears to contain a large number of carbon bonds, such -CH_3, in the film. The increased carbon and the decreased oxygen in the film also decrease the optical transmittance of the deposited film [20].

Figure 5 shows the binding peak energy of Si 2p measured by using XPS for the SiO_2 films deposited at various HMDS flow rates. The binding peak of Si 2p for SiO_2 is known to be at 103.3 eV [21] and, as shown in the figure, with increasing HMDS flow rate from 100 to 200 sccm, the peak binding energy of Si 2p increased from 102.9 eV to 103.3 eV and showed a binding energy similar to that of SiO_2. However, increasing the HMDS flow rate to higher than 400 sccm changed the binding energy from 103.3 eV back to 102.9 eV. The binding peak energy of Si 2p related to Si-OH bonding is 104.3 eV [22,23] and the energy related to SiO-$(CH_3)_x$ bonding is around 101.63 eV [24]. Therefore, the initial increase in the silicon binding peak from 102.9 eV to 103.3 eV with increasing HMDS flow rate appears to be from increased of Si-OH bonding in the films and the decreased silicon binding peak, back to 102.9 eV, for high HMDS flow rates appears to be from a significant increase in Si-$(CH_3)_x$ in the film [24].

Figure 6 shows the SEM pictures of the SiO_2 thin film deposited at HMDS flow rates of (a) 100 sccm, (b) 200 sccm, (c) 400 sccm and (d) 500 sccm. The SiO_2 films were deposited on glass substrates and the thicknesses of the SiO_2 films were maintained at 200 nm. As shown in the figure, increasing the HMDS flow rate caused a higher surface roughness of the deposited SiO_2. Especially, for HMDS flow rates higher than 400 sccm, circular protrusions with diameters of 0.9 $\sim$ 1.3 μm were observed, so the surface roughness was very high compared to the SiO_2 deposited at lower HMDS flow rates.

The increased surface roughness with increasing HMDS flow rate is believed to be related to increased Si-$(CH_3)_x$ (x = 1, 2 or 3) incorporated into the SiO_2 film due to the incomplete dissociation of HMDS, as observed in the FT-IR data. The Si-$(CH_3)_x$ dissociated in the plasma can form particles easily by colliding with other Si-$(CH_3)_x$ in the plasma due to the extremely small mean free path during the AP-PECVD processing. These particles can be deposited on the SiO_2 and increase the surface roughness of the SiO_2. If the surface roughness and Si-$(CH_3)_x$ bonding in the SiO_2 film deposited at high HMDS flow rates are to be decreased, a higher oxygen flow rate is needed for the further dissociation of Si-$(CH_3)_x$. Therefore, an optimized condition having a high SiO_2 deposition rate with a low level of impurities and a low surface roughness is believed to be obtained by controlling the ratio of the oxygen flow rate to the HMDS flow rate.

IV. CONCLUSIONS

SiO_2 thin film was deposited by using a modified DBD-type AP-PECVD system for various HMDS flow rates in a gas mixtures of HMDS + Ar + O_2 at temperatures lower than 50 °C and the characteristics of deposited thin film were studied to investigate the possibility of

depositing SiO_2-like thin films by using AP-PECVD at temperatures lower than 50 °C. Increasing the HMDS flow rate in the gas mixture increased the deposition rate. However, it also increased impurities such as C and H in the film and the surface roughness. The impurities and the surface roughness are believed to be from the Si-$(CH_3)_x$ ($x = 1$, 2 or 3), which was incompletely dissociated from HMDS and was incorporated in the deposited film. To obtain a SiO_2 film at a high deposition rate with a low level of impurities and a low surface roughness, an adequate mixture of oxygen and HMDS appears to be needed. In this experiment, by using a HMDS flow rate lower than 200 sccm in gas mixtures of HMDS/Ar(30 slm)/O_2(30 slm), we could obtain SiO_2-like thin films having a low levels of impurities and low surface roughness. This experiment, shown that by optimizing the process conditions further, a high-purity SiO_2 thin film can be deposited on a flexible substrate, such as a polymer substrates, by using roll-to-roll AP-PECVD.

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