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Characteristics of SiO_x thin films deposited by atmospheric pressure chemical vapor deposition as a function of HMDS/O_2 flow rate

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ABSTRACT

SiO_2-like thin films were deposited using a modified dielectric barrier discharge with a gas mixture of hexamethyldisilazane (HMDS)/O_2/He/Ar and their film characteristics were investigated as functions of the HMDS and O_2 flow rates. As the HMDS flow rate was increased, higher amounts of Si–$(CH_3)_x$ bonds and lower amounts of Si–OH bonds were observed in the deposited SiO_x, due to the increase in the amount of the less dissociated HMDS, which also caused an increase of the surface roughness. The addition and increase of the oxygen flow to HMDS/He/Ar brought the stoichiometry of SiO_x close to SiO_2 and decreased the surface roughness by decreasing the amount of Si–$(CH_3)_x$ bonds through the increased decomposition and oxidation of HMDS, even though the deposition rate was decreased. However, when the O_2 flow rate was higher than a certain threshold, the surface roughness increased again, possibly due to the decrease in the extent of HMDS dissociation caused by the decreased plasma density at the higher oxygen flow rate. By using an optimized gas mixture of HMDS (150 sccm)/O_2 (14 slm)/He (5 slm)/Ar (3 slm), SiO_2-like thin films with a very low impurity level and having a smooth surface could be obtained with a deposition rate of approximately 42.7 nm/min.

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1. Introduction

Silicon dioxide (SiO_2) thin films have various industrial applications such as dielectric materials for electronic devices, corrosion protection layers for mechanical structures, passivation layers for electronic device substrates and food packing. [1–3]. These days, one of the prominent issues related to SiO_2 thin films is their application to flexible substrates, which requires processing at a low process temperature along with good film properties.

For the deposition of SiO_2 thin films on a substrate at a low temperature, various physical and chemical vapor deposition methods, such as low pressure plasma enhanced chemical vapor deposition (LP-PECVD), atmospheric pressure CVD (APCVD) [4], sputter deposition, evaporation, ion beam assisted evaporation, etc., have been studied. However, most of these techniques use a vacuum for the deposition of SiO_2 thin films on the substrates. Therefore, when SiO_2 thin films are formed on flexible substrates, their production cost increases very rapidly with increasing substrate width, especially at widths larger than a meter.

Recently, atmospheric pressure plasma enhanced CVD (AP-PECVD) has been investigated for the deposition of various materials, including SiO_2 thin films on flexible substrates, for use as dielectric materials, permeation barrier materials, etc. [5]. As the plasma source of the AP-PECVD for large area processing, a dielectric barrier discharge (DBD), which is a glow type discharge, is generally used, because of its good plasma uniformity over a large substrate area [6,7]. The use of atmospheric pressure plasma processes makes it very easy to shuttle the substrates from one process to another, because they do not require a vacuum chamber or a load-lock, thus leading to a lower equipment footprint and appreciable cost reduction. Hence, this method is more useful for large scale substrates than other processes. However, the deposition rate afforded by conventional DBD-type AP-PECVD is generally low, due to the low plasma density, especially at substrate temperatures lower than 100°C, which are required for flexible substrate and organic device processing, and their operation in an atmospheric pressure plasma can cause particle problems in addition to substrate damage by arcing when the substrate is located between the two electrodes of the DBD-type plasma system.

In this study, an AP-PECVD inline-system having a modified DBD source and a multi-pin type power electrode was used to deposit SiO_x thin films at a low temperature without damaging the substrate and at a high deposition rate. Previously, the characteristics of SiO_2 deposited by a remote-type DBD source with a multi-pin power electrode were investigated, however a low deposition rate with high surface roughness was observed [8]. The low deposition rate and high surface roughness were related to the feed gas flow configuration. In this experiment, a modified discharge source having the characteristics of both remote-type and direct-type was used to increase the deposition

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rate and limit the damage to the substrate. In addition, a gas suction system was installed in the AP-PECVD and the effect of the HMDS and O_2 flow rates on the deposition characteristics of SiO_2 was further investigated to obtain optimized film characteristics.

2. Experiment

A schematic diagram of the experimental setup used to deposit the SiO_2 films is shown in Fig 1. The DBD source consisted of three flat-ground metal electrodes and two multi-pin power electrodes providing low breakdown voltages and higher plasma densities at the same applied voltage, as demonstrated in a previous study [9]. All of the electrodes were covered with 3 mm ceramic plates and one of the ground electrodes (60 mm × 130 mm × 40 mm) was located at the center area between the two power electrodes (25 mm × 130 mm × 40 mm), while the other two ground electrodes (25 mm × 130 mm × 20 mm) were located at the bottom below the substrate.

Atmospheric pressure plasmas were generated by applying 30 kHz 5 kV AC power to the multi-pin electrodes. As the silicon precursor, HMDS (Sigma-Aldrich Co, purity 99.9%, $Si_2NH(CH_3)_6$) was used and was delivered to the system using He as a carrier gas. A gas mixture composed of HMDS(delivered by He)/O_2/He(5 slm)/Ar (3 slm) was used to deposit the SiO_2 thin films, where the mixture of He/Ar was used as the discharge gas and O_2 was used for the oxidation of HMDS. HMDS and O_2/He(5 slm)/Ar (3 slm) were separately fed onto the surface of the sample through the ground electrode at the center of the system to reduce the number of particles on the substrate through the homogenous reaction of HMDS with oxygen. The reacted gas mixture was also exhausted through the other sidewall of the power electrodes by a suction mechanism. The samples were processed under atmospheric pressure and at room temperature without heating, even after their exposure to the plasma. In addition, to separate the discharge gas environment from the outside air environment, a nitrogen gas curtain system was attached, as shown in Fig. 1.

The thickness of the deposited film was measured using a step profilometer (Tencor, Alpha step 500) and the chemical bonding states of the films were measured by X-ray photoelectron spectroscopy (XPS; Thermo Electronics, Multilab ESCA2000) and Fourier transform infrared spectrometry (FTIR; Bruker IFS-66/S). An Mg source was used as the X-ray source for XPS. The surface charging during XPS analysis was corrected by shifting the C 1 s peak to 284.5 eV. The surface roughness and/or particles on the deposited SiO_x thin film were observed by field emission scanning electron microscopy (Hitachi, S-4700).

3. Results and discussion

Fig. 2 shows the deposition rate of SiO_x measured as a function of the HMDS (at a fixed O_2 flow rate of 14 slm) and O_2 (at a fixed HMDS flow rate of 150 sccm) flow rates, while the flow rates of He/Ar and AC voltage were maintained at He (5 slm)/Ar (3 slm) and 5 kV, respectively. As shown in Fig. 2, increasing the HMDS flow rate from 100 to 300 sccm in the gas mixture of HMDS/He/Ar/O_2 increased the deposition rate from 27.7 ± 0.8 to 54.4 ± 0.6 nm/min, which is about 2~4 times higher than that obtained in the previous studies using a remote-type discharge source [8]. However, the deposition rate decreased almost linearly from 50 ± 1.5 to 34.9 ± 1.6 nm/min with increasing O_2 flow rate in the gas mixture. The increase of the SiO_x deposition rate with increasing HMDS flow rate is related to the increase of the silicon content in the gas mixture. However, increasing the HMDS flow rate at a fixed O_2 flow rate also increases the carbon content in the gas mixture and, therefore, the carbon percentage can be increased in the growing SiO_x thin film by increasing the HMDS flow rate. To decrease the carbon content in the growing SiO_x thin film, the O_2 flow rate needs to be increased, but as shown in the figure, increasing the O_2 flow rate at a fixed HMDS flow rate decreased the SiO_x deposition rate. The decrease of the SiO_x deposition rate observed with increasing O_2 flow rate can be explained by the following mechanisms. Assuming that the adsorption of the HMDS precursors onto the surface is the rate-limiting step, the increase of the oxygen concentration in the gas mixture would prohibit the adsorption of HMDS on the surface, resulting in the reduction of the deposition rate [10]. In addition, the excessive oxygen in the gas mixture might decrease the electron density in the plasma and induce a filamentary discharge, resulting in a decrease of the SiO_2 deposition rate, due to the decreased amount of HMDS dissociation at the lower plasma density resulting from the increased oxygen gas flow [8].

The chemical structure of the deposited SiO_x thin films was investigated using FTIR spectroscopy. Fig. 3(a) and (b) shows the FTIR spectra measured for various HMDS flow rates (O_2 at 14 slm) and for various O_2 flow rates (HMDS at 150 sccm). The other deposition parameters are the same, as shown in Fig. 2. The SiO_x thin films were deposited at a thickness of 200 nm. The strong absorption peak shown in the FTIR spectra in the range of 1082–1092 cm^{-1} is from the Si–O–Si asymmetric stretching mode. The peaks at 972–978 cm^{-1} and 3250–3600 cm^{-1} are related to the Si–OH bonding (OH broad band) [11–13], while the peaks at 850–860 cm^{-1} and 1246–1260 cm^{-1} are related to the methyl groups of the Si–$(CH_3)_3$ and Si–$(CH_3)_x$ bondings, respectively. In addition, the peak related to Si–O–C and Si–CH_2–Si was

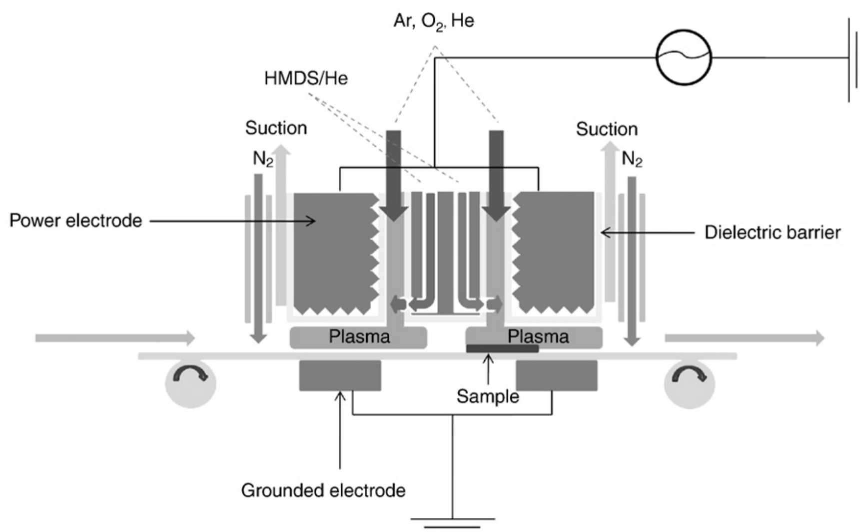

Fig. 1. Schematic diagram of the AP-PECVD in-line system with a pin-to-plate DBD-type source.

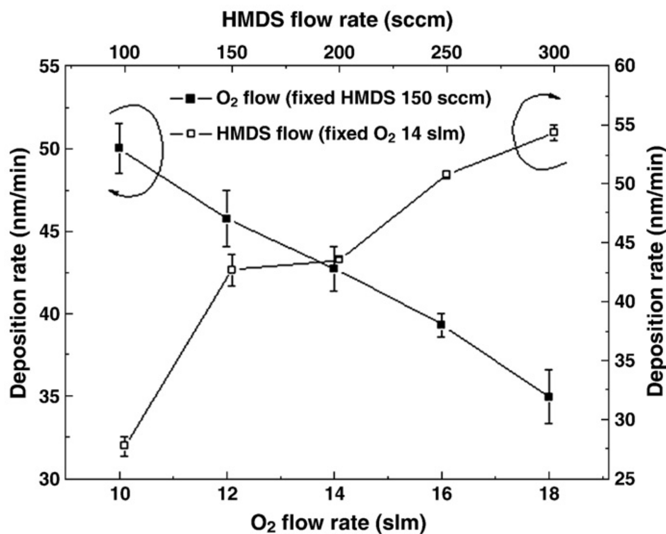

Fig. 2. Deposition rate of the SiO_x films as functions of the HMDS flow rate (the O_2 flow rate was maintained at 14slm) and O_2 flow rate (the HMDS flow rate was maintained at 150 sccm) using HMDS/O_2/He(5 slm)/Ar (3 slm) at an applied voltage of 5 kV (30 kHz).

observed at 1100 cm^{-1} [14–16], even though it was overlapped with the tail of the Si–O–Si peak. As shown in Fig. 3(a), increasing the HMDS flow rate from 100 to 300 sccm at a fixed flow rate of O_2 of 14 slm increased the bonding peaks related to Si–$(CH_3)_3$, Si–$(CH_3)_x$ and CH_x, due to the increase in the amount of carbon (or CH_x) in the gas mixture. In addition, as shown in the figure, increasing the HMDS flow rate decreased the bonding peaks related to Si–O–Si and Si–OH, due to the decrease in the amount of silicon bonding with oxygen in the deposited SiO_x thin film. Increasing the oxygen flow rate at a fixed HMDS flow rate of 150sccm, as shown in Fig. 3(b), slightly increased the bonding peaks of Si–OH and Si–O–Si, while decreasing the bond peaks related to carbon, until the oxygen flow rate approached 14 slm. However, when the oxygen flow rate was increased further to 18 slm, the bonding peaks related to Si–O–Si and Si–OH were slightly decreased, while no significant change/or a slight increase of the peaks related to carbon was observed. The increase of the bonding peak intensities related to Si–O–Si and the decrease of the peak intensities related to carbon at oxygen flow rates lower than 14 slm are related to the increased oxidation of silicon in the deposited SiO_x thin film. However, the absence of any further decrease of the peak intensities related to carbon at oxygen flow rates higher than 14 slm may be related to the decrease of the plasma density with increasing oxygen flow rate, which decreases the dissociation of HMDS and oxygen molecules in the gas mixture. When the methyl group bondings related to carbon, such as Si–$(CH_3)_3$, Si–$(CH_3)_x$, and CH_x, remain in the SiO_x film, the film density may be decreased and the characteristics of the film degraded [17]. In this experiment, a SiO_2-like film with a low carbon content appears to be obtained at an oxygen flow rate of 14 slm and HMDS flow rate of 150 sccm, in which the presence of CH_x symmetric and asymmetric stretching bands at 2900–2960 cm^{-1} with a low intensity and the absence of the other typical CH_x bands were also confirmed [18].

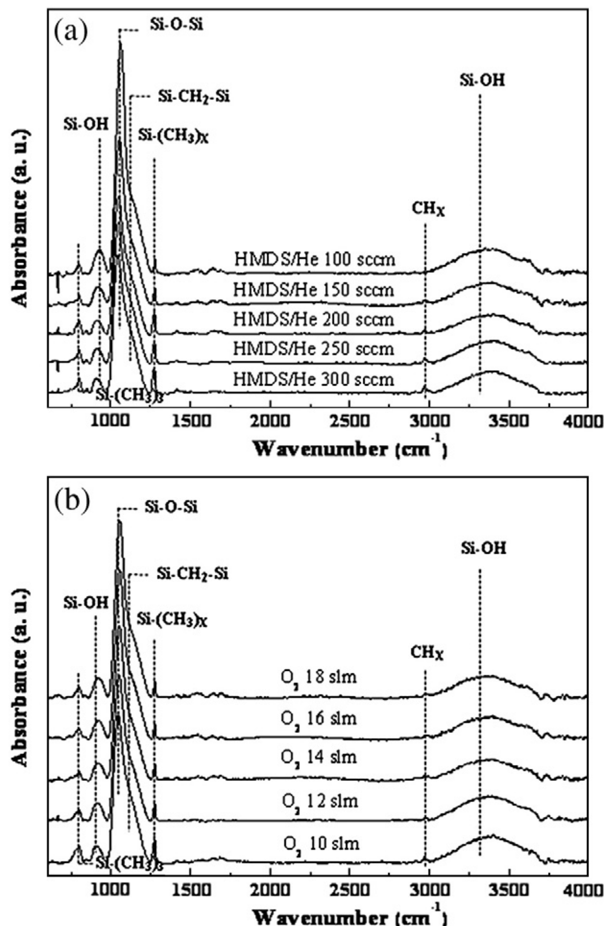

Fig. 3. FTIR spectra of the SiO_x thin films deposited at various (a) HMDS flow rates and (b) O_2 flow rates by the AP-PECVD system. The deposition conditions are the same as those shown in Fig. 2.

Using XPS, the atomic percentage ratios of each film (except for hydrogen) were investigated and the results are shown in Table 1 for the deposition conditions shown in Fig. 2. As shown in the table, increasing the HMDS flow rate from 100 to 300 sccm at a fixed oxygen flow rate of 14 slm increased the ratio of C/Si and decreased the ratio of O/Si slightly, due to the increased number of methyl groups in the deposited thin film, which is similar to the results shown in Fig. 3. Also, increasing the oxygen flow rate at a fixed HMDS flow rate of 150sccm increased the ratio of O/Si slightly and the ratio of C/Si until the oxygen flow rate reached 14 slm, possibly due to the increased incorporation of oxygen into the film caused by its increased concentration in the gas mixture. However, when the oxygen flow rate exceeded 14slm, the ratio of O/Si remained nearly unchanged and the ratio of C/Si increased again, as in the case of the results shown in Fig. 3. When the oxygen flow rate is increased, the plasma density is decreased, due to the increase in the consumption of electrons by the oxygen atoms and molecules, and the dissociation of HMDS is also decreased. The increase of the ratio of C/Si at oxygen flow rates higher than 14slm is believed to be related to the decreased dissociation of HMDS and increased incorporation of carbon into the deposited SiO_x thin film.

Table 1
Atomic percentage ratio investigated by XPS as a function of HMDS and O_2 flow rates. The deposition conditions are the same as those shown in Fig. 2.

Gas	Flow rate (sccm)	O/Si ratio	C/Si ratio
HMDS	100	2.43	0.12
	150	2.36	0.17
	200	2.32	0.25
	250	2.27	0.38
	300	2.22	0.42
Gas	Flow rate(slm)	O/Si ratio	C/Si ratio
O_2	10	2.31	0.35
	12	2.34	0.23
	14	2.36	0.17
	16	2.43	0.25
	18	2.43	0.26

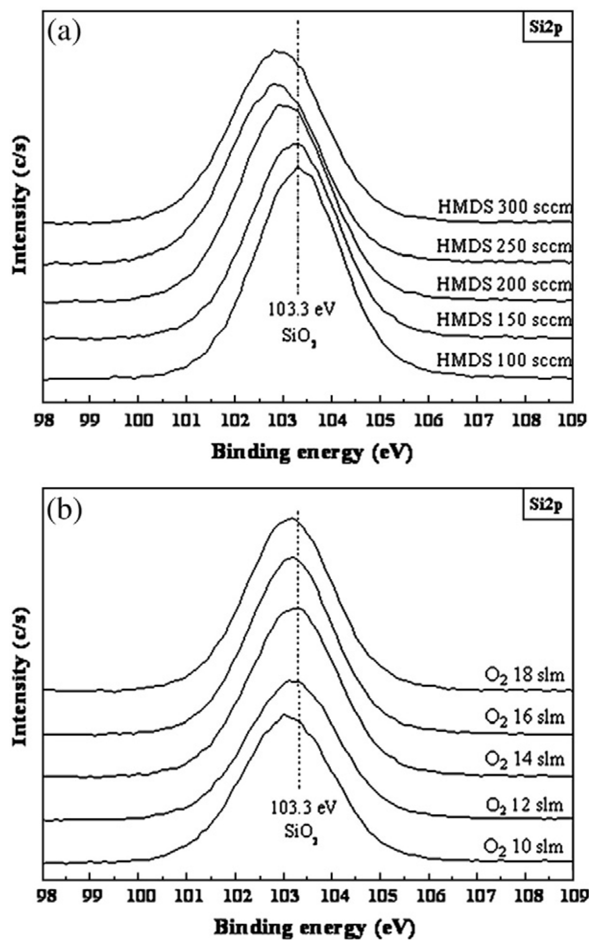

Fig. 4. Narrow scan XPS data of Si 2p measured on the SiO_x thin films deposited at various (a) HMDS flow rates and (b) O_2 flow rates. The deposition conditions are the same as those shown in Fig. 2.

Using the XPS narrow scan data, the change of the binding state of Si 2p as functions of the HMDS flow rate and O_2 flow rate was investigated for the conditions shown in Fig. 2 and the results are shown in Fig. 4(a) and (b), respectively. As shown in Fig. 4(a), increasing the HMDS flow rate from 100 to 300 sccm, while maintaining the oxygen flow rate at 14 slm, shifted the binding energy peak position of Si 2p from 103.3 eV, which is known to be the binding energy peak of thermally grown SiO_2, to a lower energy position [19]. The downfield shift of the binding energy of the Si 2p peak is due to the increased bonding of Si with the methyl group, which has lower electronegativity than oxygen [20]. When the oxygen flow rate was increased from 10 slm to 14 slm, while keeping the HMDS flow rate fixed at 150 sccm, the binding peak energy of Si 2p was shifted from 103.01 eV to 103.3 eV, which is close to the binding peak energy of SiO_2. However, further increasing the oxygen flow rate to 18slm shifted the peak energy back to the lower energy of 103.15 eV. The initial increase of the Si 2p peak with increasing oxygen flow rate up to 14slm is due to the increase of the Si bonding with oxygen and the decrease of the Si bonding with the methyl group, in addition to the increase of the Si–OH bonding (104.3 eV) [21]. However, the decrease of the Si 2p peak with the further increase of the oxygen flow rate is believed to be related to the increased bonding of Si with carbon and/or the decreased Si bonding with oxygen, due to the decreased dissociation of HMDS caused by the decreased plasma density at the higher oxygen flow rate, as mentioned above.

Fig. 5 shows the SEM micrographs of the SiO_x thin films deposited at various HMDS flow rates and O_2 flow rates. The thickness of the SiO_x thin film was maintained at 200 nm. Fig. 5(a) and (b) shows the SEM micrographs for HMDS flow rates of 150 sccm and 300 sccm, respectively, while the oxygen flow rate was maintained at 14 slm. Fig. 5(c) and (d) shows the SEM micrographs for oxygen flow rates of 10 slm and 18 slm, respectively, while the HMDS flow rate was maintained at 150 sccm. As shown in the SEM micrographs, when the HMDS flow rate is higher than the optimized HMDS flow rate of 150 sccm at an oxygen flow rate of 14 slm, an increase of the surface roughness caused by an increase in the number of small bumps was

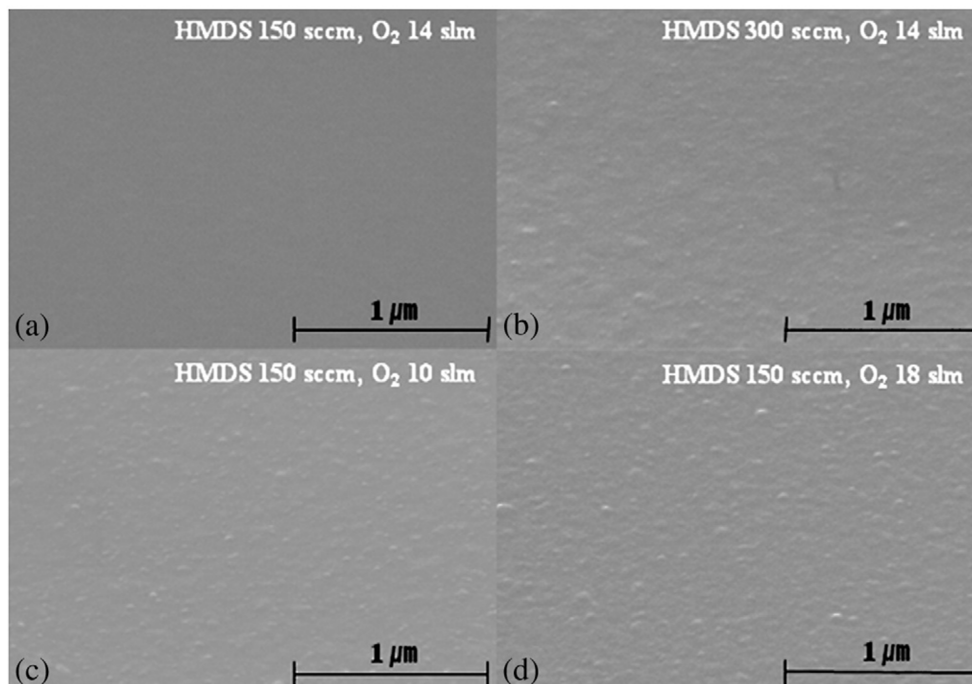

Fig. 5. SEM micropraphs of the deposited SiO_x thin films : (a) for HMDS (150 sccm) and O_2 (14 slm), (b) for HMDS (300 sccm) and O_2 (14 slm), (c) for HMDS (150 sccm) and O_2 (10 slm), and (d) for HMDS (150 sccm) and O_2 (18 slm). The other deposition conditions are the same as those in Fig. 2.

observed. When the oxygen flow rate was lower or higher than 14 slm at a fixed HMDS flow rate of 150 sccm, as shown in Fig. 5(c) and (d), respectively, an increase of the surface roughness was also observed. These small bumps observed are believed to be related to the methyl groups in the film. Therefore, by optimizing the oxygen flow rate and HMDS flow rate, a SiO_2-like thin film with a smooth surface could be obtained.

4. Conclusion

In this study, SiO_x thin films were deposited, using a gas mixture of HMDS/O_2/He (5 slm)/Ar (3 slm) and 5 kV 30 kHz AC power in an AP-PECVD system with a modified pin-to-plate DBD source having the combined characteristics of both the remote-type and the direct-type. This discharge source was equipped with a gas suction system and N_2 gas curtain system attached to the discharge source. As the HMDS flow rate was increased at a fixed oxygen flow rate, the deposition rate of the SiO_x thin film increased, however the surface roughness was increased by the formation of methyl groups such as Si–$(CH_3)_3$, Si–$(CH_3)_x$, and CH_x in the deposited SiO_x thin film. When the oxygen flow rate was increased at a fixed HMDS flow rate, the deposition rate decreased with increasing oxygen flow rate, possibly due to the decrease of the adsorption rate of Si on the surface and the decrease in the dissociation of HMDS caused by the decreased plasma density. When the oxygen flow rate was varied at a fixed HMDS flow rate, an increase in the surface roughness was observed due to the methyl groups remaining in the deposited SiO_x thin film, except when the optimized oxygen flow rate was used. As a result, a smooth SiO_2-like film was deposited at a rate of about 42.7 nm/min under the optimized conditions of an HMDS flow rate of 150 sccm and O_2 flow rate of 14 slm, while flowing He(5 slm)/Ar(3 slm) and applying 5 kV 30 kHz AC power.

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