



Atmospheric pressure PECVD of SiO₂ thin film at a low temperature using HMDS/O₂/He/Ar

Y.S. Kim^a, J.H. Lee^a, J.T. Lim^a, J.B. Park^b, G.Y. Yeom^{a,b,*}

^a Department of Advanced Materials Science & Engineering, Sungkyunkwan University, Chunchun-Dong 300, Jangan-Gu, Suwon 440-746, Republic of Korea

^b SKK Advanced Institute of Nano Technology, Sungkyunkwan University, Chunchun-Dong 300, Jangan-Gu, Suwon 440-746, Republic of Korea

ARTICLE INFO

Available online 4 February 2009

Keywords:

Atmospheric pressure
Deposition
Silicon dioxide
Hexamethyldisilazane (HMDS)

ABSTRACT

SiO₂-like thin films were deposited at a low temperature (<50 °C) by a remote-type, atmospheric pressure plasma enhanced chemical vapor deposition (AP-PECVD) using a pin-to-plate-type, dielectric barrier discharge with gas mixtures containing hexamethyldisilazane (HMDS)/O₂/He/Ar. The film characteristics were investigated according to the HMDS and O₂ flow rates. To obtain a more SiO₂-like thin film, an adequate combination of HMDS and oxygen flow rates was required to remove the -(CH₃)_x bonding in the HMDS and to oxidize the Si in HMDS effectively. At the optimized flow rates, the surface roughness of the SiO₂-like thin film was also the lowest. By using HMDS (50 sccm) and O₂ (500 sccm) flow rates in the gas mixture of HMDS/O₂/He (2 slm)/Ar (600 sccm), SiO₂-like thin films with a low impurity (<6.35% C) were obtained at a deposition rate of approximately 10.7 nm/min.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

SiO₂ thin film is an important material with many applications such as a barrier layer for food packaging, corrosion protection layer, water permeation barrier for organic electronics, and dielectric material for electronic devices [1]. In such applications, a critical issue for industry application is achieving low cost deposition of SiO₂ films with high quality and on a large scale.

For the deposition of SiO₂ thin films, plasma enhanced chemical vapor deposition (PECVD) is quite suitable for the production of high-quality thin films at a low temperature [2,3]. However, PECVD requires an expensive vacuum system because it is operated at low pressures. Due to this limitation in low-pressure PECVD, interest has focused on the development of non-thermal plasma sources operating at atmospheric pressure that would be suitable for CVD technology [4].

Among the non-thermal plasma sources operating at atmospheric pressure, direct-type dielectric barrier discharges (DBDs) have been investigated for various applications including surface modifications by locating the substrate to be treated between the two electrodes covered by the dielectric material. However, arcing is frequently observed during the operation of the direct-type DBD and the substrate is more likely to be damaged during the processing [5].

Therefore, in this study, a remote-type DBD was used to deposit SiO₂-like thin film at a low temperature to prevent possible damage to

the surface of the substrates during atmospheric pressure plasma processing. Especially, to generate high-density plasma at low breakdown voltages, a pin-to-plate-type DBD consisting of a multi-pin power electrode instead of a planar power electrode was used [6]. As the precursor of Si, hexamethyldisilazane (HMDS) was used and the effect of the HMDS and oxygen flow rates on the deposited SiO₂-like film characteristics were investigated.

2. Experimental

Fig. 1 shows a schematic diagram of the atmospheric pressure PECVD (AP-PECVD) system with the remote-type DBD source used in this experiment for the deposition of SiO₂ at low temperature. The DBD source was composed of a multi-pin power electrode in the center and two blank, ground metal electrodes facing and equidistant from the two sidewalls of the power electrode, which produced two adjacent, linear plasma sources located nearly vertically above the substrate. The power electrode, shown in Fig. 1, comprised a multi-pin-type electrode instead of a blank electrode to enable operation at low breakdown voltage and to produce higher plasma densities at the same applied voltage, as determined in previous study [6].

The remote-type, pin-to-plate DBDs were generated by applying 5 kV AC voltage to the power electrode at a frequency of 25 kHz. The gas was fed into the system through the gap between the sidewalls of the power electrode and ground electrodes. 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%, Si₂NH(CH₃)₆) was used as the Si precursor. HMDS was fed into the system by bubbling He through the HMDS liquid reservoir kept at 65 °C. HMDS was used as the Si

* Corresponding author. SKK Advanced Institute of Nano Technology, Sungkyunkwan University, Chunchun-Dong 300, Jangan-Gu, Suwon 440-746, Republic of Korea. Tel.: +82 31 299 6562; fax: +82 31 299 6565.

E-mail address: gyyeom@skku.edu (G.Y. Yeom).

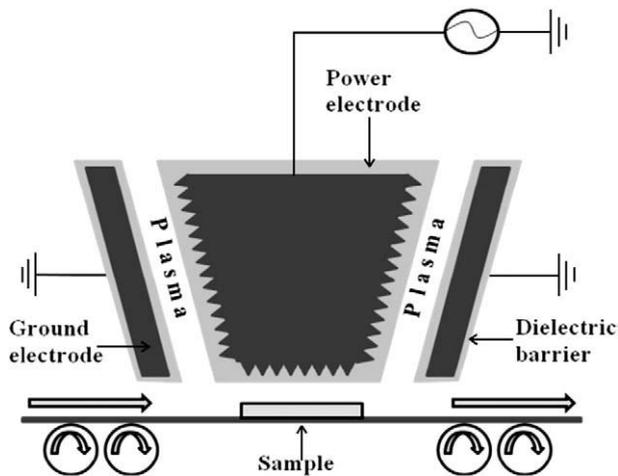


Fig. 1. Schematic diagram of the remote type, AP-PECVD in-line system.

precursor because it is relatively safe, non-corrosive, and has been widely used in the integrated circuit industry as a photoresist adhesion-promoting agent [7]. In addition, the SiO_2 thin film produced with HMDS is known to have lower porosity than the films grown using other silicon precursors such as tetramethylcyclotetrasiloxane, tetraethoxysilane, and tetramethyldisiloxane.

Silicon wafers were used as the substrates, a gas mixture composed of HMDS/ O_2 /He (2 slm)/Ar (600 sccm) was used to deposit the SiO_2 thin films, He/Ar was used as the discharge gas and O_2 was used for the oxidation of HMDS. The samples were processed at room temperature without heating ($<50^\circ\text{C}$ even after the plasma exposure). In order to investigate the characteristics of the thin film, the HMDS (bubbles by He) and O_2 flow rates were varied from 40 to 90 sccm and from 500 sccm to 900 sccm, respectively, while the other process parameters were fixed.

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 X-ray photoelectron spectroscopy (XPS; Thermo Electronics, Multilab ESCA2000). The chemical bonding states of the deposited SiO_2 film were investigated by Fourier transform infrared spectrometry (FT-IR; Bruker IFS-66/S) and by XPS. The surface

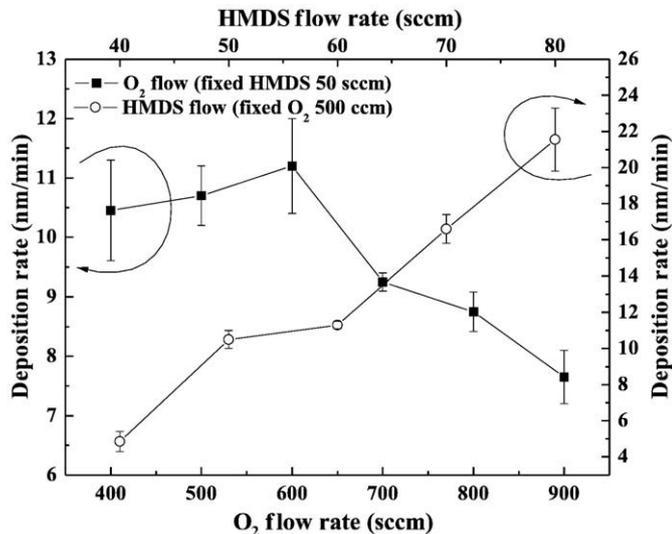


Fig. 2. Deposition rate of the SiO_x films as a function of HMDS rate and O_2 flow rates using HMDS/ O_2 /He (2 slm)/Ar (600 sccm) at an applied voltage of 5 kV (25 kHz). O_2 and HMDS flow rates were maintained at 500 and 50 sccm, respectively.

morphology of the thin films was observed by a field emission scanning electron microscope (FE-SEM; Hitachi, S-4700).

3. Results and discussion

Fig. 2 shows the deposition rate of SiO_x measured as a function of HMDS (at 500 sccm of O_2) and O_2 (at 50 sccm of HMDS) flow rates in HMDS/ O_2 /He (2 slm)/Ar (600 sccm) and at 5 kV of 25 kHz AC voltage. As shown in the figure, the increase of HMDS flow rate from 50 sccm to 80 sccm at the fixed O_2 flow rate increased the deposition rate almost linearly from 4.9 ± 0.6 nm/min to 21.6 ± 1.8 nm/min. When the O_2 flow rate was increased from 400 sccm to 900 sccm at the fixed HMDS flow rate of 50 sccm, the deposition rate was initially increased from 10.5 ± 0.9 nm/min to 11.2 ± 0.8 nm/min with the increase of O_2 flow rate up to 600 sccm, but then decreased to 7.7 ± 0.5 nm/min with the further increase of O_2 flow rate to 900 sccm. The increased deposition rate with increasing HMDS flow rate at a fixed O_2 flow rate was attributed to the increased silicon content in the gas mixture with increasing HMDS flow rate, which increased the decomposed silicon from HMDS by the plasma [8]. However, an increased HMDS flow rate at a fixed O_2 flow rate can increase the impurities such as carbon and hydrogen in the deposited thin film due to the deposition of silicon from HMDS without completely removing the $-\text{CH}_x$ bonding by oxidation. The initial increase of deposition rate with increasing O_2 flow rate at a fixed HMDS flow rate was related to the increased decomposition of HMDS by oxidation. However, at an O_2 flow rate

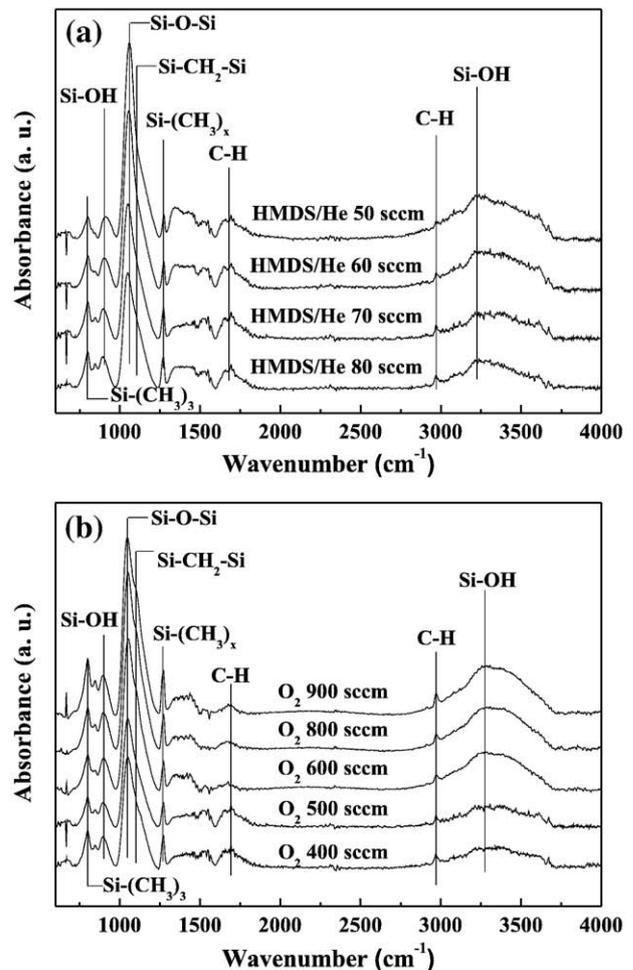


Fig. 3. FT-IR spectra of the SiO_x deposited at different (a) HMDS and (b) O_2 flow rates by AP-PECVD. The deposition conditions are the same as those shown in Fig. 2.

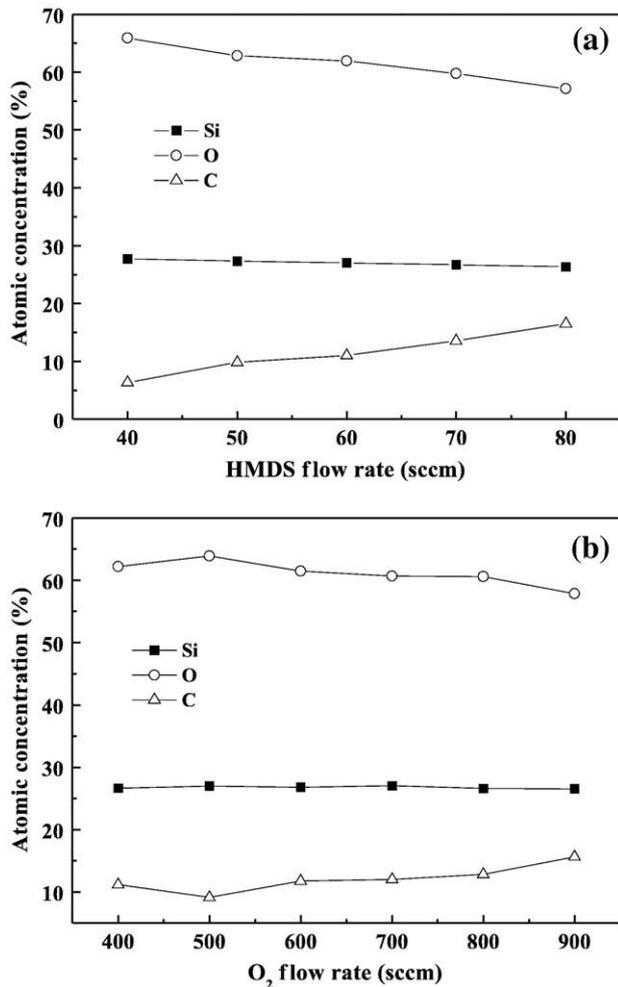


Fig. 4. XPS spectra of Si 2p core levels of the SiO_x thin films as a function of the (a) HMDS and (b) O₂ flow rates. The deposition conditions are the same as those in Fig. 2.

higher than 600 sccm, the plasma became unstable and a filamentary discharge was observed with the decreased plasma density. Therefore, the decreased deposition rate when the O₂ flow rate was higher than 600 sccm was attributed to the decrease of HMDS dissociation due to the decreased plasma density.

Using FT-IR, the binding states of the deposited thin films were investigated for the samples deposited as a function of the HMDS rate and O₂ flow rates, shown in Fig. 2, and the results are shown in Fig. 3(a) and (b), respectively. The SiO_x thin films were deposited on 200-nm-thick silicon wafers at room temperature. As shown in the figure, the absorption peak related to Si–O–Si bonding was observed at 1082–1092 cm⁻¹ [9], the peaks related to Si–OH bonding were observed at 972–978 cm⁻¹ [10] and 3250–3600 cm⁻¹ (OH broad band) [11], the peak related to Si–(CH₃)₃ bonding at 850–860 cm⁻¹ [12], and the peak related to Si–(CH₃)_x at 1246–1260 cm⁻¹ [13]. In addition, the peak related to Si–O–C and/or Si–CH₂–Si was observed at 1100 cm⁻¹ [14], even though this peak was overlapped with the tail of the Si–O–Si peak. As shown in Fig. 3(a), the increase of HMDS flow rate from 50 sccm to 80 sccm at a fixed O₂ flow rate increased the bonding peaks related to Si–(CH₃)_x and Si–(CH₃)₃ due to the incomplete decomposition of HMDS (Si₂NH(CH₃)₆) induced by the increased HMDS flow rate. In addition, due to the decreased recombination of the dissociated HMDS with oxygen, the bonding peaks related to Si–O–Si and Si–OH were decreased with the increased HMDS flow rate. The increased Si–(CH₃)_x and Si–(CH₃)₃ in the deposited SiO_x thin film can decrease the density of the film [15]. When the oxygen flow rate was varied at a fixed HMDS flow rate as shown in Fig. 3(b), the bonding peaks related

to Si–(CH₃)_x and Si–(CH₃)₃ were slightly decreased as the oxygen flow rate was increased from 400 sccm to 500–600 sccm. However, these peaks were increased with further increase of the oxygen flow rate. On the other hand, the peaks related to Si–O–Si and Si–OH were increased steadily with increasing oxygen flow rate. The initial decrease of Si–(CH₃)_x and Si–(CH₃)₃ as the oxygen flow rate was increased to 500–600 sccm was related to the increased oxidation of dissociated HMDS. However, the increase of Si–(CH₃)_x and Si–(CH₃)₃ with the further increase of oxygen flow rate was attributed to the formation of a filamentary discharge observed at an oxygen flow rate of 600 sccm and higher, and which decreased the plasma density. However, the increase of oxygen in the gas mixture increased Si–O–Si and Si–OH due to the increased oxidation of silicon in the dissociated HMDS.

The atomic compositions of the SiO_x thin films deposited as a function of the HMDS and O₂ flow rates in Fig. 2 were measured using XPS and the results are shown in Fig. 4(a) and (b), respectively. Due to the detection limit of XPS, the hydrogen content in the deposited thin film could not be estimated. As shown in the figures, the silicon content in the film was not significantly affected by the variation of either flow rate and remained nearly constant at 27 ± 0.4%. However, as shown in Fig. 4(a), the increased HMDS flow rate increased the carbon percentage in the deposited film while decreasing the oxygen percentage, which was attributed to the Si–(CH₃)_x and Si–(CH₃)₃ bonding observed by FT-IR. These impurities also decreased the optical transmittance [16]. When the oxygen flow rate was increased, the oxygen percentage was maximized and the carbon percentage was minimized at an oxygen flow rate of 500 sccm (approximately at 500–

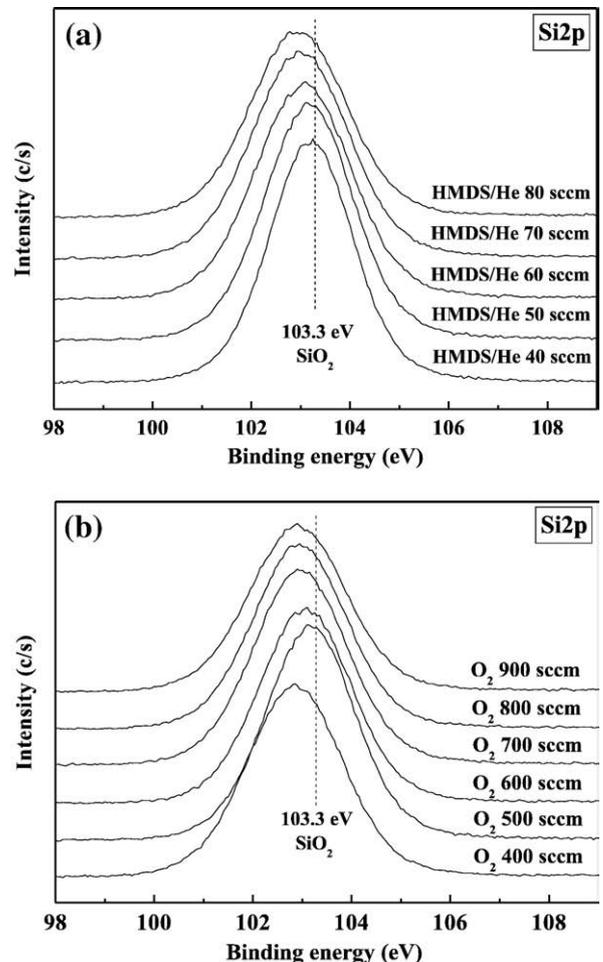


Fig. 5. Atomic composition of thin films deposited at different (a) HMDS and (b) O₂ flow rates, as measured by XPS. The deposition conditions are the same as those in Fig. 2.

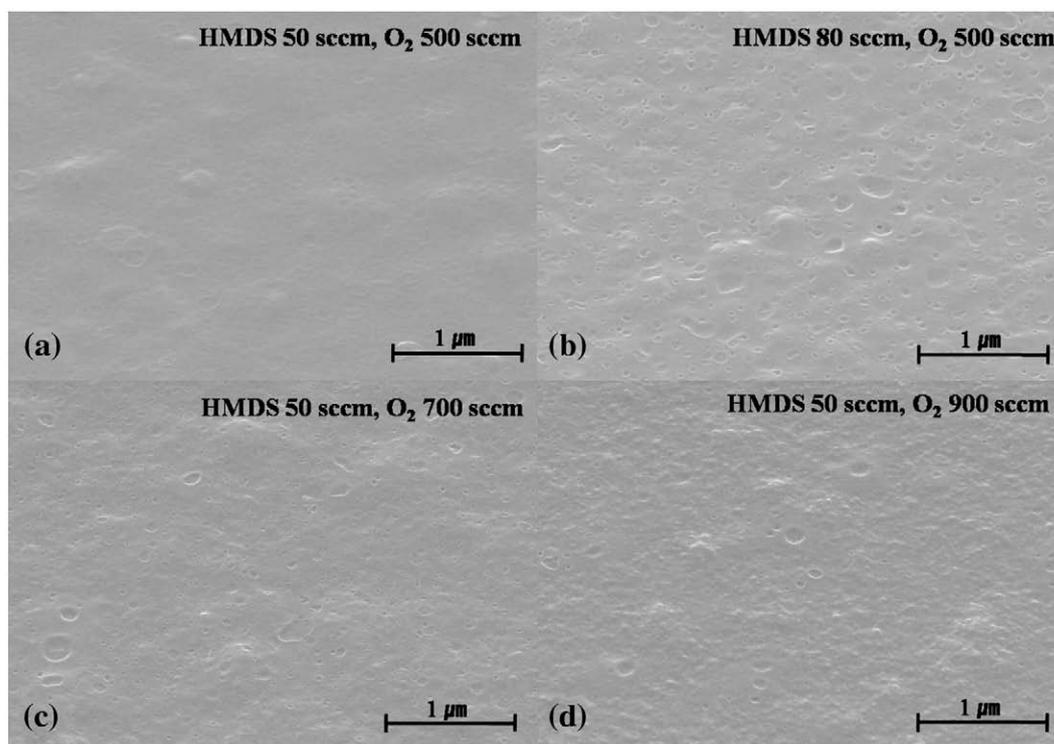


Fig. 6. SEM micrographs of the deposited films: (a) HMDS (50 sccm)/O₂ (500 sccm), (b) HMDS (80 sccm)/O₂ (500 sccm), (c) HMDS (50 sccm)/O₂ (700 sccm), and (d) HMDS (50 sccm)/O₂ (900 sccm). The deposition conditions are the same as those in Fig. 2.

600 sccm). The further increase of oxygen flow rate increased the carbon percentage and decreased the oxygen percentage in the deposited film. The highest oxygen percentage with the lowest carbon percentage at 500 sccm was related to the optimized oxygen percentage that increased the oxidation of dissociated HMDS without forming the filamentary discharge that occurred at high oxygen flow rate due to the increased electron attachment to oxygen. At an O₂ flow rate of 500 sccm, the oxygen and carbon percentages were 63.9% and 9.1%, respectively. As shown in Fig. 2, the deposition rate was close to a maximum at this condition.

The binding peaks of Si 2p of the SiO_x thin films deposited as a function of HMDS and O₂ flow rates were also observed by XPS and the results are shown in Fig. 5(a) and (b), respectively. As shown in Fig. 5(a), the increase of HMDS flow rate from 40 sccm to 80 sccm shifted the binding peak of Si 2p from 103.3 eV, which is the binding energy of Si 2p for thermally grown SiO₂ thin film [17], to a lower binding energy due to the increase of Si-(CH₃)_x and Si-(CH₃)₃ in the deposited thin film in addition to Si-O [18]. On the contrary, when the oxygen flow rate was increased at a fixed HMDS flow rate, as shown in Fig. 5(b), the initial increase of oxygen flow rate from 400 sccm to 500 sccm increased the binding peak of Si 2p close to that of SiO₂, due to the increased oxidation of dissociated HMDS. However, with further increase in the oxygen flow rate, the binding peaks were shifted to lower binding energies due to the decreased dissociation of HMDS caused by the decreased plasma density. The binding energy peak of Si 2p, observed at oxygen and HMDS flow rates of 500 and 50 sccm, respectively, was close to that of thermally grown SiO₂ and appeared to show the optimized SiO₂ deposition condition.

The surfaces of the SiO_x thin films deposited as a function of HMDS and O₂ flow rates were observed with SEM and the results are shown in Fig. 6(a)–(b) for the former and Fig. 6(a), (c)–(d) for the latter, respectively. As shown in the figure, the increase of HMDS flow rate from 50 sccm to 80 sccm increased the surface roughness so that craters sized 0.05 μm–0.2 μm could be observed on the surface. These craters appeared to be related to the Si-(CH₃)₃, Si-(CH₃)_x group in the film that tended to decrease the density of the film and increase the

porosity [19]. When the O₂ flow rate was increased from 500 sccm to 900 sccm while the HMDS flow rate was maintained at 50 sccm, the surface roughness was also increased as evidenced by the appearance of small protrusions in addition to the craters. These small protrusions were attributed to the increase of Si-OH bonding which also increased the film porosity. However, under the optimized condition of HMDS (50 sccm)/O₂ (500 sccm) flow rate, the surface with the lowest roughness was obtained despite the surface roughness not being completely smooth.

4. Conclusions

In this study, SiO_x thin films were deposited with gas mixtures composed of HMDS/O₂/He (2 slm)/Ar (600 sccm) using an AP-PECVD system with remote-type DBD source and 5 kV 25 kHz AC power. Increasing HMDS flow rate in the gas mixture increased the deposition rate but more impurities such as Si-(CH₃)₃, Si-(CH₃)_x were introduced in the deposited film due to the incomplete decomposition of HMDS and the surface roughness was also increased. When the O₂ flow rate was increased at a constant HMDS flow rate, the deposition rate was maximized at 600 sccm. Furthermore, the lowest Si-(CH₃)₃ and Si-(CH₃)_x, and the smoothest surface were obtained near the 600 sccm. An excessively high oxygen content in the gas mixture formed a filamentary discharge which decreased the dissociation of HMDS, while an excessively low oxygen content decreased oxidation of dissociated HMDS. Therefore, an optimized SiO_x deposition condition, close to thermal SiO₂, was obtained at an HMDS flow rate of 50 sccm and an oxygen flow rate of 500 sccm.

Acknowledgements

This research was supported by a grant (F0004041-2008-31) from the Information Display R&D Center, one of the 21st Century Frontier R&D Programs funded by the Ministry of Knowledge Economy (MKE) and the Korea Industrial Technology Foundation (KOTEF) through the Human Resource Training Project for Strategic Technology.

References

- [1] X. Zhu, F.A. Khonsari, C.P. Etienne, M. Tatoulian, *Plasma Process. Polym.* 2 (2005) 407.
- [2] K.L. Choy, *Prog. Mater. Sci.* 48 (2003) 57.
- [3] H.O. Pierson, *Handbook of Chemical Vapor Deposition Principles, Technology Application*, William Andrew Publishing, New York, 1999 Noyes.
- [4] J.H. Lee, Thuy T.T. Pham, Y.S. Kim, J.T. Lim, S.J. Kyung, G.Y. Yeom, *J. Electrochem. Soc.* 155 (2008) D163–D166.
- [5] J.B. Park, S.J. Kyung, G.Y. Yeom, *Jpn. J. Appl. Phys.* 46 (2007) L942.
- [6] Y.H. Lee, S.J. Kyung, C.H. Jeong, G.Y. Yeom, *Jpn. J. Appl. Phys.* 44 (2005) L47.
- [7] D. Freeman, W. Kern, *J. Vac. Sci. Technol. A* 7 (1989) 1446.
- [8] G.R. Nowling, M. Yajima, S.E. Babayan, M. Miravej, X. Yang, W. Hoffman, R.F. Hicks, *Plasma Sources Sci. Technol.* 14 (2005) 477.
- [9] Q. Chen, Y. Zhang, E. Han, Y. Ge, *J. Vac. Sci. Technol., A* 24 (6) (2006).
- [10] F. Massines, N. Gherardi, A. Fornelli, S. Martin, *Surf. Coat. Technol.* 200 (2005) 1855.
- [11] N. Mutsukura, K. Akita, *Thin Solid Films* 349 (1999) 115.
- [12] Y. Sawada, S. Ogawa, M. Kogoma, *J. Phys. D-Appl. Phys.* 28 (1995) 1661.
- [13] K. Schmidt-Szalowski, Z. Rzanek-Boroch, J. Sentek, Z. Rymuza, Z. Kusznierevicz, M. Misiak, *Plasma Polym.* 5 (2000) 173.
- [14] D. Trunec, Z. Navratil, P. Stahel, L. Zajickova, V. Bursikova, J. Cech, *J. Phys. D: Appl. Phys.* 37 (2004) 2112.
- [15] S.E. Alexandrov, N. McSparran, L. Michael, Hichman, *Chem. Vap. Depos.* 11 (2005) 481.
- [16] T. Gunji, Y. Makabe, N. Takamura, Y. Abe, *Appl. Organomet. Chem.* 15 (2001) 683.
- [17] J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, *Handbook of X-ray Photoelectron Spectroscopy*, Pekin-Elmer Co., Minesota, 1992, p. 45.
- [18] L.A. O'Hara, B. Parbhoo, S.T. Leadley, *Surf. Interface Anal.* 36 (2004) 1427.
- [19] A. Milella, M. Creatore, M.A. Blauw, M.C.M. van de Sanden, *Plasma Process. Polym.* 4 (2007) 621.