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Characteristics of SiO_x Thin Film Deposited by Atmospheric Pressure Plasma-Enhanced Chemical Vapor Deposition Using $PDMS/O_2/He$

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Silicon oxide thin films were deposited using a modified, pin-to-plate, dielectric barrier discharge system with polydimethylsiloxane (PDMS), bubbled by He/O_2 gas mixtures at atmospheric pressure and a temperature of less than 50°C. Increasing PDMS flow rate in the gas mixture increased the deposition rate, but also increased the surface roughness due to the formation of particles in the gas phase as a result of increased PDMS and silanol groups, leading to incomplete decomposition or oxidation of PDMS. The increase in the ratio of oxygen flow rate to PDMS flow rate decreased the surface roughness with increasing deposition rate due to the efficient oxidation of PDMS. However, when the oxygen flow rate was raised above 1 slm, due to the increased oxidation of PDMS in the gas phase and the decreased PDMS dissociation by the decreased plasma density, the surface roughness was again increased with decreasing deposition rate. At the gas mixture of 9 slm PDMS/He and 1 slm oxygen, a smooth, SiO_2-like thin film was obtained at a deposition rate of 12 nm/min.
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Atmospheric pressure, plasma-enhanced chemical vapor deposition (AP-PECVD) processes are recognized as promising and cost-effective methods for wide-area coating on sheets of steel, glass, polymeric web, etc. To reduce the production cost of large-area electronic devices such as flat-panel display devices and thin-film photovoltaics, it is desirable to develop alternative deposition processes that operate at atmospheric pressure and utilize in-line processing.

SiO_2 layers have a wide variety of electronic applications such as gate dielectrics, insulators, and waveguides.[1,2] In addition to electronic applications, SiO_2 layers are routinely applied to polymers to reduce the water vapor and oxygen permeation into versatile polymeric materials.[3] AP-PECVD has been used for the low temperature deposition of SiO_2 thin films on thermally sensitive materials such as flexible displays, organic light-emitting diode, and organic thin-film transistors due to the difficulty of depositing SiO_2 thin film on these materials at high temperatures.

AP-PECVD of SiO_2 at low temperature involves the dissociation of volatile silicon precursors/oxygen with plasma and the formation of SiO_2 onto the substrate surface.[4,5] Organo-silicon precursors are advantageous precursors for PECVD of silicon compounds because of the increased safety of manufacturing (in comparison with silane) arising from the stability, low flammability, and low toxicity of these compounds.[6,7] When PECVD is used for SiO_2 formation, the increased pressure can form unwanted solid particles which deposit from the gas phase, thereby reducing the transparency of the deposited films.[8] Chemically, more reactive precursors are found to produce far more particles as a result of significant polymerization reactions and subsequent powder formation in the gas phase.[9] For example, organo-silicon precursors such as tetramethylcyclotetrasiloxane, octamethylcyclotetrasiloxane, polyhydrogenmethysiloxane, and tetramethyldisiloxane are known to show a serious particle problem during the deposition of SiO_2 by AP-PECVD. However, compared to other organo-silicon precursors, polydimethylsiloxane (PDMS) is known to exhibit superior material properties in addition to fewer particle problems, possibly due to the lower chemical reactivity of PDMS during the deposition with a dielectric barrier discharge (DBD-type) AP-PECVD source.[10,11]

In this study, SiO_2 thin films were deposited using a modified DBD called a "pin-to-plate-type DBD" to generate high density plasma with a gas mixture of $PDMS/O_2$. The effect of the gas mixture on the physical and chemical properties of SiO_2 was investigated. The pin-to-plate DBD used in this study had a lower breakdown voltage and a higher plasma density than the conventional DBD at the same applied voltage due to the high electric field at the multiple pins of the power electrode.[12]

Experimental

Figure 1 shows the AP-PECVD in-line system used for the deposition of SiO_2. The discharge system was composed of a multipin top electrode and a flat-ground electrode separated by about 8 mm. Both electrodes were covered with a 3 mm thick ceramic plate and had dimensions of 198 mm long × 105 mm wide. Atmospheric pressure plasmas were generated by applying 5 kV ac power (25 kHz) to the multipin electrode. At that condition, the power consumed in the glow discharge was about 258.3 ± 7 W. The substrate temperature was maintained below 50°C using a chiller. The process gas was fed into the system through the shower holes in the ceramic material of the power electrodes. PDMS prepolymer and curing agent (Sylgard 184, Dow Corning) were used as the Si precursors. The chemical structure of PDMS is composed of repeating $–OSi(CH_3)_2O–$ units.[13] The PDMS prepolymer and curing agent (prepolymer: curing agent = 10:1) were fed into the system by bubbling He gas through the PDMS liquid reservoir kept at room temperature.

To optimize the characteristics of the thin film, the PDMS and O_2 flow rates were varied from 7 to 15 slm and from 0.6 to 1.4 slm,

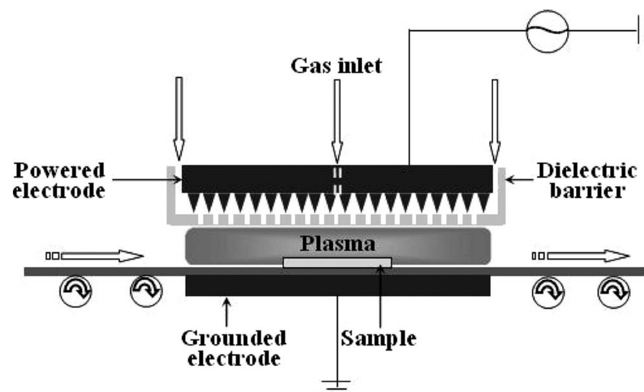

Figure 1. Schematic diagram of the AP-PECVD in-line system (pin-to-plate DBD type).

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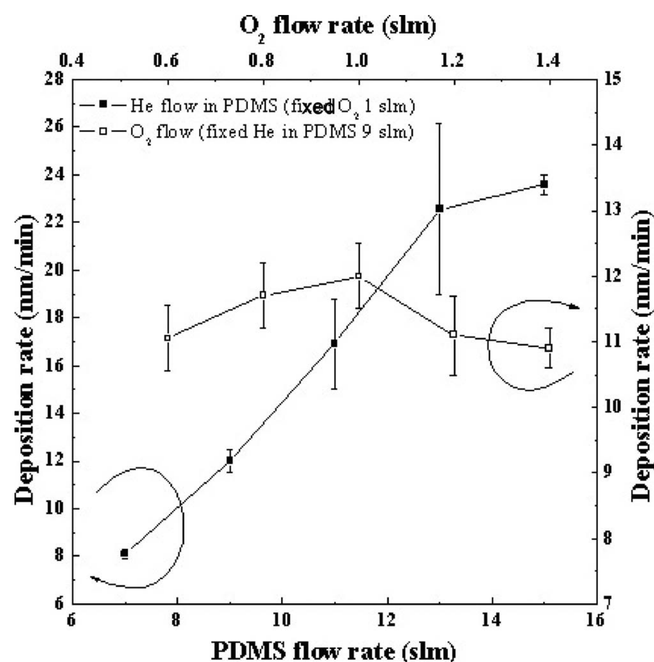

Figure 2. Deposition rate of silicon oxide films as a function of PDMS and O_2 flow rates using PDMS (bubbled by He)/O_2 at an applied voltage of 5 kV (25 kHz). When the PDMS flow rate was varied, the oxygen flow rate was maintained at 1.0 slm, and when the oxygen flow rate was varied, the PDMS flow rate was maintained at 9.0 slm.

respectively, while the other process parameters were fixed. During the deposition, the substrates were fed into the plasma at the line speed of 0.3 m/min.

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

Results and Discussion

Figure 2 shows the deposition rate of SiO_2 measured as a function of PDMS (bubbled by He at room temperature) and O_2 gas flow rates. Glass was used as the substrate and was kept at a temperature of less than 50°C. As shown in the figure, when the PDMS flow rate was increased from 7 to 15 slm while the O_2 gas flow rate was maintained at 1 slm, the deposition rate was increased almost linearly from 8.1 ± 0.2 to 23.6 ± 0.4 nm/min. The increased deposition rate was related to the increased silicon source in the gas mixture due to the increased PDMS flow rate and was, therefore, related to the increased reaction of silicon with oxygen in the gas mixture. When the oxygen flow rate was increased from 0.6 to 1 slm while the PDMS flow rate was kept at 9 slm, the deposition rate was increased from 11.05 ± 0.5 to 12 ± 0.5 nm/min, but then decreased to 10.9 ± 0.3 nm/min when the O_2 gas flow rate was further increased to 1.4 slm. The initial increase in deposition rate as the O_2 gas flow rate was increased to 1 slm was attributed to the increased oxidation of PDMS and was therefore believed to be related to the increased decomposition of PDMS by oxygen for the formation of silicon oxide in the film.[14] However, the decrease in deposition rate with further increase in O_2 gas flow rate above 1 slm was attributed to the decrease in the dissociation of PDMS due to the decreased plasma density. At an oxygen flow rate above 1 slm, the plasma became unstable by showing a filamentary-type discharge and the plasma density was decreased by the significant increase of electron attachment to the oxygen atoms as a result of the increased level of O_2 gas in the gas mixture. The decreased electron density in the plasma decreased the dissociation of the PDMS, and thereby decreased the deposition rate when the O_2 gas flow surpassed the critical value of 1 slm.

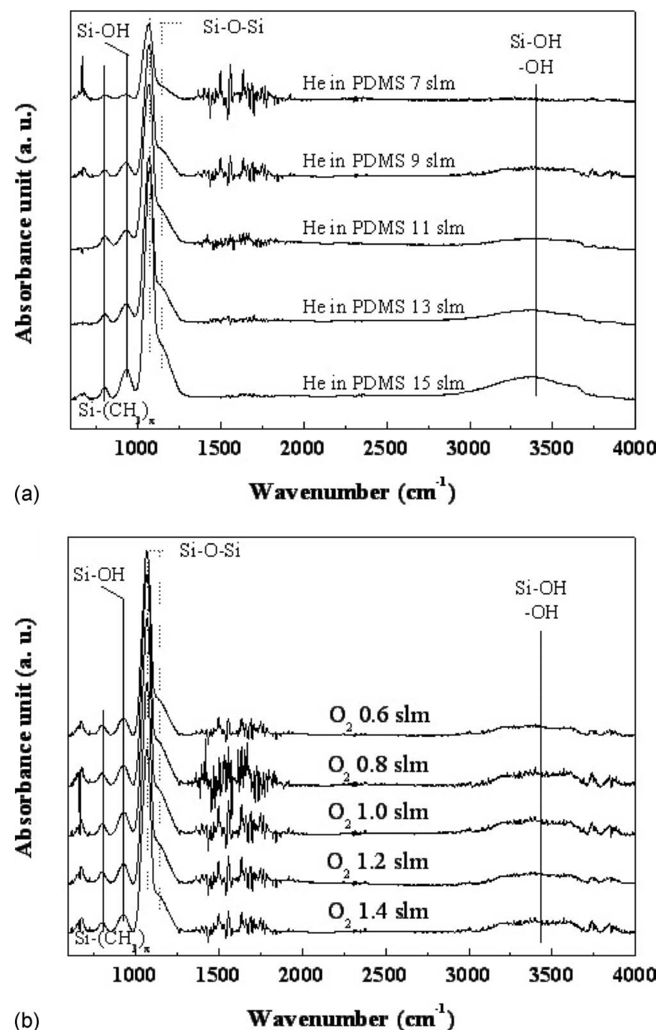

Figure 3. FTIR spectra of silicon oxide deposited at different (a) PDMS and (b) O_2 gas flow rates by AP-PECVD. The deposition conditions are the same as those in Fig. 2.

The chemical structure of the deposited SiO_2 thin films was investigated using FTIR spectroscopy. Figure 3a and b shows the FTIR spectra measured for various PDMS flow rates (O_2 at 1 slm) and for various O_2 flow rates (PDMS at 9 slm), respectively. The SiO_2 thin films were deposited on p-type ⟨100⟩ silicon wafers and the thickness of the thin film was maintained at 200 ± 25 nm. As shown in Fig. 3a, as the PDMS flow rate increased from 7 to 15 slm, the peak intensities related to the Si–O–Si bonding, located at the wavenumber ranges of 1000–1100[15] and 1500 cm^{-1},[16] and to the Si–OH bonding, located at the wavenumber ranges of 925–930 and 3350–3650 cm^{-1},[16] increased. Also, the increased PDMS flow rate increased the peak intensities related to the Si–$(CH_3)_x$ bonding located at 801 cm^{-1}.[17] However, when the O_2 gas flow rate was increased from 0.6 to 1.4 slm, as shown in Fig. 3b, the observed bonding peak intensities related to the Si–O–Si bonding, Si–$(CH_3)_x$ bonding, and Si–OH bonding did not change significantly. The increase of the Si–OH bonding peak with increas-

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Table I. Composition of the silicon oxide thin films deposited as a function of the PDMS and O_2 flow rates measured by XPS (the hydrogen content was not included due to XPS detection limit).

Gas	Flow rate (slm)	Silicon	Oxygen	Carbon
PDMS	7	29.8	68.9	1.4
	9	30.2	68.3	1.5
	11	28.9	68.9	2.3
	13	29.8	67.6	2.6
	15	29.9	67.1	3.0
O_2	0.8	28.9	69.4	1.7
	1	30.2	68.3	1.5
	1.2	30.2	67.6	2.2
	1.4	29.9	68.1	2.0

ing PDMS flow rate suggested the presence of a high silanol group,[18] $[-O_nSi(OH)_{4-n}-]_n$, in the film, thereby possibly indicating the higher hydrophilic property and higher porosity of the deposited film.[13] The increase of the Si–$(CH_3)_x$ bonding peak with increasing PDMS flow rate indicated the possible formation of a soft rather than hard film. The increase of both Si–OH and Si–$(CH_3)_x$ bonding peaks with increasing PDMS flow rate was attributed to the insufficient oxidation of the dissociated PDMS.

Using the XPS wide-scan data, the composition of the films deposited as a function of the PDMS and O_2 gas flow rates shown in Fig. 3 was estimated and the results are shown in Table I. As shown in the table, the composition did not vary significantly with PDMS and O_2 flow rates, and the carbon content was generally low.

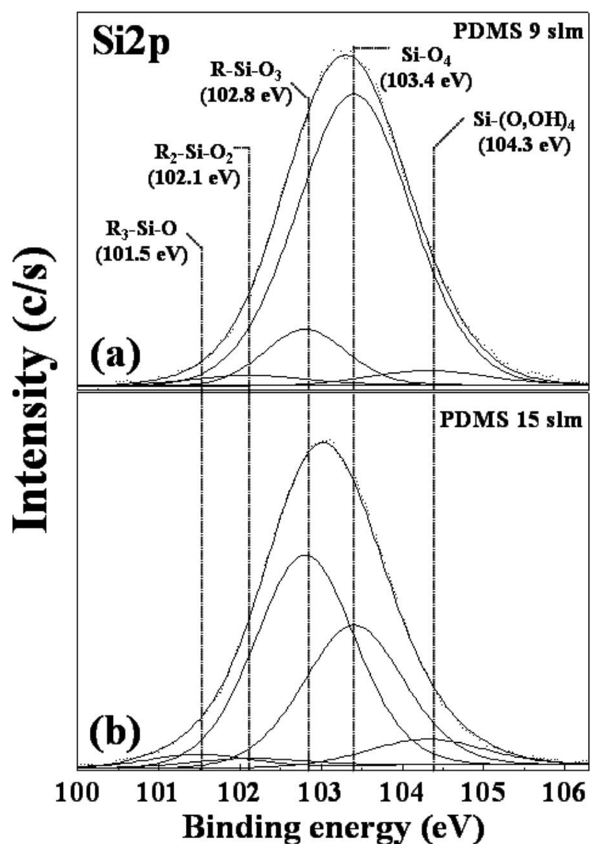

Figure 4. XPS narrow-scan data of the Si 2p peaks of silicon oxide thin films deposited as a function of the PDMS flow rate: (a) 9.0 and (b) 15 slm. The deposition conditions are the same as those in Fig. 2.

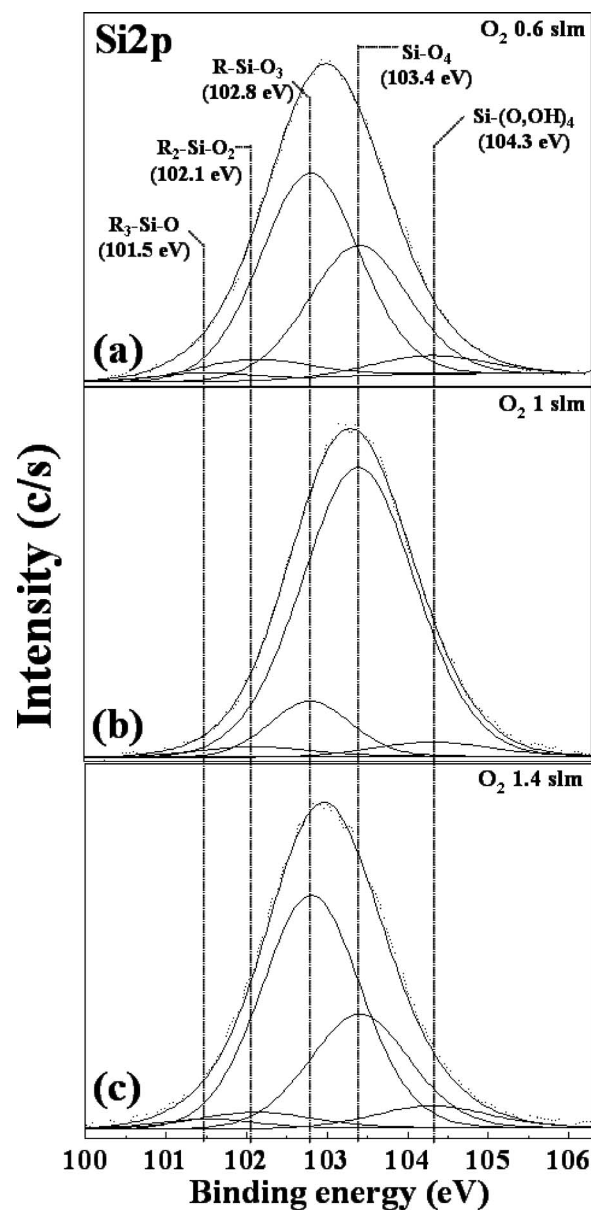

Figure 5. XPS narrow-scan data of the Si 2p peaks of silicon oxide thin films deposited as a function of the O_2 flow rate: (a) 0.6, (b) 1.0, and (c) 1.4 slm. The deposition conditions are the same as those in Fig. 2.

However, as shown in the table, the carbon percentage increased from 1.4 to 3.0% as the PDMS flow rate increased from 7 to 15 slm due to the increase of Si–$(CH_3)_x$ bonding in the film. The carbon content as a function of the O_2 flow rate was minimized at 1.0 slm of O_2, possibly due to the optimized oxidation and dissociation of PDMS.

Using the XPS narrow-scan data, the bonding states of silicon in the deposited films were investigated. Figure 4a and b shows the XPS narrow-scan data of Si 2p measured for the samples in Fig. 3a deposited at PDMS flow rates of 9 and 15 slm, respectively. The Si 2p peak locations were calibrated by positioning the C 1s peak at 284.5 eV. As shown in the figures, the peak location of Si 2p decreased from 103.28 to 103.08 eV when the PDMS flow rate increased from 9 to 15 slm. The Si 2p peaks can be deconvoluted to a few peaks related to silicon binding to R [R = methyl group $(-CH_3)_x$: R–Si–O_3: 102.8 eV, R_2–Si–O_2: 102.1 eV, R_3–Si–O: 101.5 eV], Si–O_4 (SiO_2, 103.4 eV), and Si–$(O,OH)_4$ (104.3 eV).[19,20] The deconvoluted results are also shown in the fig-

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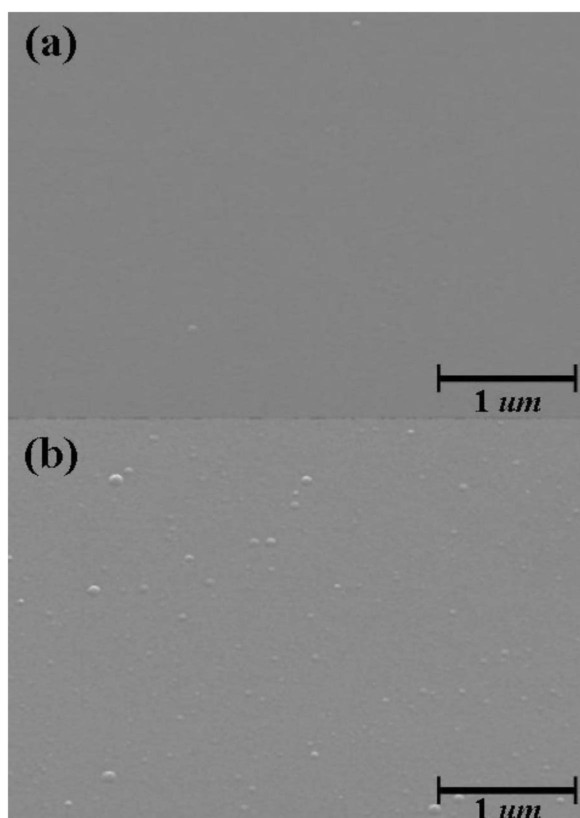

Figure 6. SEM micrographs of silicon oxide thin films deposited as a function of the PDMS flow rate: (a) 9.0 and (b) 15 slm. The deposition conditions are the same as those in Fig. 2.

ures. As shown in the figures, the silicon binding peak containing SiO_2 decreased, while the peak containing R–Si–O_3 increased when the PDMS flow rate increased from 9 to 15 slm. Also, the silicon binding peak containing Si–$(O,OH)_4$ increased with increasing PDMS flow rate. The silicon binding peaks related to R_3–Si–O and R_2–Si–O_2 showed very low peak intensities at both PDMS flow rates of 9 and 15 slm. The very low silicon binding peak intensities related to R_3–Si–O and R_2–Si–O_2 were believed to be attributed to the relatively high dissociation of PDMS under our experimental condition. However, the increase of the peak related to R–Si–O_3 binding observed with increasing PDMS flow rate appeared to show the reduced oxidation of the dissociated PDMS with increased PDMS flow rate. The increase of the silicon binding peak containing Si–$(O,OH)_4$ observed with increased PDMS flow rate was also related to the incomplete PDMS oxidation.[20]

Figure 5a-c shows the XPS narrow-scan data of Si 2p measured for the samples in Fig. 3b deposited with O_2 gas flow rates of 0.6, 1, and 1.4 slm, respectively. Each Si 2p peak was deconvoluted similarly to the related binding peaks shown in Fig. 4. As shown in the figures, the silicon binding peak intensities related to R_3–Si–O, R_2–Si–O_2, and Si–$(O,OH)_4$ were low and did not change significantly with increasing O_2 flow rate, which was similar to the result presented in Fig. 3b. However, for the silicon binding peaks related to SiO_2 and R–Si–O_3, at an O_2 gas flow rate of 1 slm, a maximum peak was obtained for the peak related to SiO_2, while a minimum peak was obtained for the silicon binding peak related to R–Si–O_3. These two peaks were believed to be related to the highest efficiency of gas dissociation and oxidation of PDMS at an O_2 flow rate of 1 slm. That is, at an O_2 flow rate of less than 1 slm, Si–$(CH_3)_x$ bonding remained in the film due to the insufficient oxidation of dissociated PDMS. However, at an O_2 flow rate of more than 1 slm,

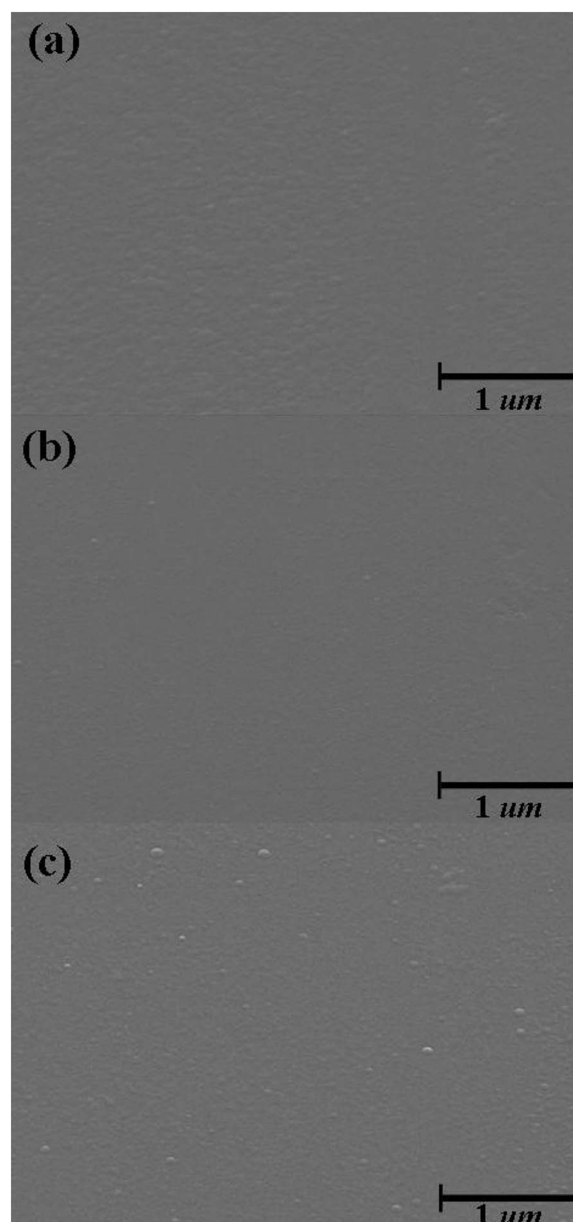

Figure 7. SEM micrographs of silicon oxide thin films deposited as a function of the O_2 flow rate: (a) 0.6, (b) 1.0, and (c) 1.4 slm. The deposition conditions are the same as those in Fig. 2.

the dissociation of PDMS decreased and the Si–$(CH_3)_x$ bonding again increased due to the decreased plasma density resulting from the formation of unstable plasma.

The surface morphology of the thin film deposited as a function of PDMS and O_2 gas flow rates was investigated by scanning electron microscopy (SEM) and the results are shown in Fig. 6 and 7, respectively. Figure 6a and b shows the results for PDMS flow rates of 9 and 15 slm, respectively, while the O_2 gas flow rate was kept at 1 slm. Figure 7a-c shows the results for O_2 gas flow rates of 0.6, 1, and 1.4 slm, respectively, while the PDMS flow rate was kept at 9 slm. The thickness of the deposited thin film was maintained at 200 nm. As shown in Fig. 6, the surface roughness increased as the PDMS flow rate increased from 9 to 15 slm, particularly as it increased from 13 to 15 slm, possibly due to particle formation in the gas phase resulting from homogeneous condensation reactions or due to porosity in the thin film resulting from the increased Si–$(OH)_x$ bonding in the film with the increased PDMS flow rate

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(data not shown). Also, when the thin film was scratched with tweezers, the film deposited at a higher PDMS flow rate was more easily scratched by the increased Si–$(CH_3)_x$ bonding, indicating the formation of a soft thin film which is unsuitable as a water-permeation diffusion barrier.[21]

For the thin film deposited as a function of O_2 gas flow rate, the increase of O_2 gas flow rate from 0.6 to 1 slm decreased the surface roughness so that a very smooth film surface with nearly no particles on the surface was obtained at the latter O_2 gas flow rate, as shown in Fig. 7b. The roughness of the 0.6 slm O_2 film was attributed to the insufficient oxidation of PDMS due to the insufficient oxygen in the gas mixture. However, the surface roughness again increased as the O_2 flow rate was increased above 1 slm, which was attributed to the gas-phase oxidation of PDMS leading to particle formation. Also, in this experiment, even though some particles were observed on the deposited SiO_2 surface for some of the conditions, when comparing with the SiO_2 deposited using hexamethyldisilazane obtained by a previous experiment,[21] a smoother thin film could be obtained possibly due to the characteristics of PDMS having less chemically reactive precursors.

Conclusion

A silicon oxide thin film was deposited using a pin-to-plate, DBD-type, AP-PECVD with a PDMS (prepolymer: curing agent = 10:1) polymer source/O_2 gas at a substrate temperature lower than 50°C, with varying PMDS and O_2 gas flow rates.

The increase of PDMS (bubbled through He flow at room temperature) at a fixed O_2 gas flow rate increased the deposition rate due to the increased silicon source availability that was induced by the increased PDMS flow rate. However, the surface roughness also increased with increasing PDMS flow rate at a fixed O_2 gas flow rate, which was attributed to the increased porosity in the film as seen by the increased Si–(OH) bonding in the film, in addition to the possible particle formation in the gas phase by a homogeneous reaction. When the O_2 gas flow rate was varied at a fixed PDMS flow rate, the deposition rate peaked at a certain O_2 flow rate, at which point the surface roughness was minimized, possibly due to the optimum dissociation and oxidation of PDMS having the lowest Si–(OH) bonding in the film. At an ac power of 5 kV (25 kHz) and at a gas flow rate of PDMS (9 slm bubbled by He)/O_2 1 slm, a SiO_2-like thin film with a low carbon content of 1.5% and a smooth surface was obtained at a deposition rate of 12 nm/min.

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References

1. J. S. Jung, J. Y. Kwon, Y. S. Park, D. Y. Kim, H. S. Cho, K. B. Park, W. Xianyu, H. Yin, and T. Noguchi, *J. Korean Phys. Soc.*, **45**, S861 (2004).
2. J. Y. Lee and S. H. Lee, *J. Korean Phys. Soc.*, **45**, 558 (2004).
3. A. Gruniger and P. R. von Rohr, *Surf. Coat. Technol.*, **174**, 1043 (2003).
4. M. A. Liberman and A. J. Lichtenberg, *Principles of Plasma Discharges and Materials Processing*, Wiley Interscience, New York (1994).
5. J. H. Lee, C. H. Jeong, J. T. Lim, V. A. Zavaleyev, S. J. Kyung, and G. Y. Yeom, *Jpn. J. Appl. Phys., Part 1*, **45**, 8430 (2006).
6. K. Schmidt-Szalowski, Z. Rzanek-Boroch, J. Sentek, Z. Rymuza, Z. Kusznierewicz, and M. Misiak, *Plasmas Polym.*, **5**, 173 (2000).
7. J. H. Lee, C. H. Jeong, H. B. Kim, J. T. Lim, S. J. Kyung, and G. Y. Yeom, *Thin Solid Films*, **515**, 917 (2006).
8. Y. Sawada, S. Ogawa, and M. Kogoma, *J. Phys. D*, **28**, 1661 (1995).
9. S. R. Coulson, I. S. Woodward, J. P. S. Badyal, S. A. Brewer, and C. Willis, *Langmuir*, **16**, 6287 (2000).
10. D. R. Lide, *Handbook of Chemistry and Physics*, 76th ed., CRC, Boca Raton, FL (1995).
11. L. O'Neill, L. A. O'Hare, S. R. Leadley, and A. J. Goodwin, *Chem. Vap. Deposition*, **11**, 477 (2005).
12. Y. H. Lee, S. J. Kyung, C. H. Jeong, and G. Y. Yeom, *Jpn. J. Appl. Phys., Part 2*, **44**, L78 (2005).
13. D. C. Duffy, J. C. McDonald, O. J. A. Schueller, and G. M. Whitesides, *Anal. Chem.*, **70**, 4974 (1998).
14. J. Pulpytel, F. Arefi-Khonsari, and W. Morscheidt, *J. Phys. D*, **38**, 1390 (2005).
15. G. R. Nowling, M. Yajima, S. E. Babayan, M. Moravej, X. Yang, W. Hoffman, and R. F. Hicks, *Plasma Sources Sci. Technol.*, **14**, 477 (2005).
16. F. Massines, N. Gherardi, A. Fornelli, and S. Martin, *Surf. Coat. Technol.*, **200**, 1855 (2005).
17. D. Trunec, Z. Navratil, P. Stahel, L. Zajickova, V. Bursikova, and J. Cech, *J. Phys. D*, **37**, 2112 (2004).
18. L.-Y. Chen and F. C.-N. Hong, *Appl. Phys. Lett.*, **82**, 3526 (2003).
19. M. R. Alexander, R. D. Short, F. R. Jones, W. Michaeli, and C. J. Blomfield, *Appl. Surf. Sci.*, **137**, 179 (1999).
20. J. Viard, E. Beche, D. Perarnau, R. Berjoan, and J. Durand, *J. Eur. Ceram. Soc.*, **17**, 2025 (1997).
21. J. H. Lee, Thuy T. T. Pham, Y. S. Kim, J. T. Lim, S. J. Kyung, and G. Y. Yeom, *J. Electrochem. Soc.*, **155**, D163 (2008).

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