



Characteristics of SiO₂-Like Thin Film Deposited by Atmospheric-Pressure PECVD Using HMDS/O₂/Ar

J. H. Lee, Thuy. T. T. Pham, Y. S. Kim, J. T. Lim, S. J. Kyung, and G. Y. Yeom^z

Department of Advanced Materials Science and Engineering, Sungkyunkwan University,
Suwon 440-746, Korea

SiO₂-like thin films were deposited at low temperatures (<50°C) by atmospheric-pressure plasma-enhanced chemical vapor deposition using a pin-to-plate-type dielectric barrier discharge with a gas mixture containing hexamethyldisilazane (HMDS)/Ar/O₂. The deposition rate increased with increasing concentration of HMDS in the gas mixture. However, a powdery film with Si-OH bonding, high roughness, and low transmittance was obtained, which was attributed to the enhanced homogeneous reaction with increasing HMDS. The increase in O₂ flow rate at a fixed HMDS flow rate increased the reaction rate of the remaining HMDS on the substrate surface, which resulted in an increase in deposition rate until the remaining HMDS had completely reacted. An increase in the oxygen flow rate also increased the surface roughness and decreased the optical transmittance slightly, possibly due to the formation of small SiO₂ particles in the gas phase during the dissociation of the gas mixture under high-oxygen-percentage conditions. At the optimum condition of HMDS (15 sccm)/O₂ (300 sccm)/Ar (2 slm), smooth SiO₂-like thin films with a transmittance >95% could be obtained with a deposition rate of approximately 21 nm/min. © 2007 The Electrochemical Society. [DOI: 10.1149/1.2822963] All rights reserved.

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SiO₂ thin films have a wide variety of electronic applications such as gate dielectrics, insulators, waveguides, etc.^{1,2} In addition to electronic applications, SiO₂ thin films have been used as a diffusion barrier in various plastic packaging materials.³ They have also been investigated for applications as a diffusion barrier material for organic electronics such as organic light-emitting diodes (OLEDs) and organic thin-film transistors (OTFTs), flexible displays, etc., which are vulnerable to the environment.

For the deposition of SiO₂ thin films, chemical vapor deposition (CVD) is quite suitable for the production of high-quality thin films for a wide variety of electronic applications.^{4,5} In particular, plasma-enhanced CVD (PECVD) has been used for the low-temperature coating of SiO₂ thin films on thermally sensitive materials such as flexible displays, OLEDs, OTFTs, etc., due to the difficulty of depositing materials on these substrates at high temperatures. This low-temperature process involves the dissociation of volatile precursors with plasma and directing the reactive mixture onto the substrate surface.^{6,7} However, PECVD requires an expensive vacuum system because it is operated at low pressures. This is particularly a problem when PECVD is used to deposit uniform films on an extremely large area substrate, such as flat-panel displays and flexible displays for the next generation, due to the difficulty in generating uniform plasma over a large area.

Due to the above limitations of low-pressure PECVD, there has been considerable interest in the development of nonthermal plasma sources operating at atmospheric pressure that would be suitable for use with CVD technologies. Among the various plasma sources operating at atmospheric pressure, dielectric barrier discharge (DBD) is one of the most promising sources for generating nonequilibrium plasmas for atmospheric-pressure PECVD (AP-PECVD) processes. In recent years, laboratory- and semi-industrial-scale experiments have demonstrated the interesting capabilities of this technology for in-line deposition.^{8,9} In particular, atmospheric-pressure plasmas are being investigated for application to various flat-panel display processing such as substrate dry cleaning, photoresist ashing, dry etching, the deposition of organic and inorganic materials for diffusion barriers, etc.^{10,11}

In this study, SiO_x thin films were deposited at low temperatures (<50°C) using a modified DBD called "pin-to-plate-type DBD" for the generation of high-density plasma and with a gas mixture of hexamethyldisilazane (HMDS)/Ar/O₂. In addition, the characteris-

tics of the deposited films were investigated as a function of the HMDS and O₂ flow rates for potential application to thin-film diffusion barrier materials.

Experimental

Figure 1 shows the AP-PECVD in-line system used to deposit the SiO_x films at temperatures <50°C. The discharge system consisted of a multipin top-powered electrode and a flat ground electrode separated by approximately 8 mm, with both electrodes covered with an insulating ceramic plate (pin-to-plate DBD). The size of the electrode was 198 mm length × 105 mm width. The pin-to-plate DBD had a lower breakdown voltage and higher plasma density compared to the conventional DBD under the same applied voltage due to the strong electric field at the multiple pins of the power electrode.¹²

Atmospheric-pressure plasma discharges were generated by applying 12 kV ac power (25 kHz) to the multipin electrode. The substrate temperature was maintained at <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. HMDS [Sigma-Aldrich Co., purity 99.9%, Si₂NH(CH₃)₆] was used as the Si precursor because the glass film produced with HMDS contains significantly less OH and has higher porosity than the films grown using the other silicon precursors, such as tetramethylcyclotetrasiloxane, tet-

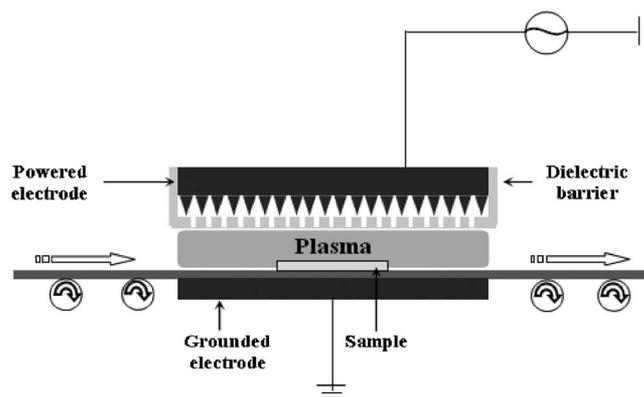


Figure 1. Schematic diagram of the AP-PECVD in-line system (pin-to-plate DBD type).

^z E-mail: gyyeom@skku.edu

Table I. Process parameters used in the deposition of SiO₂.

| | |
|------------------------------|-------------------------------|
| Substrate | Si wafer, glass |
| Gas chemistry | HMDS/Ar + Ar + O ₂ |
| Deposition temperature | <50°C |
| AC voltage | 12 kV |
| Bubbler temperature | 60°C |
| Line speed | 0.3 m/min |
| Flow rate of Ar flow in HMDS | 8–38 sccm |
| Flow rate of Ar | 2 slm |
| Flow rate of O ₂ | 300–500 sccm |

raethoxysilane, tetramethyldisioxane, etc.¹¹ In addition, HMDS was fed into the system by bubbling Ar through the HMDS liquid reservoir kept at 60°C.

Silicon wafers or glass were used as substrates, and gas mixtures of Ar/HMDS/O₂ were used to deposit the SiO_x thin films. In order to optimize the characteristics of the thin film, the HMDS flow rate (bubbled by Ar) was varied from 8 to 38 sccm and the O₂ flow rate was varied from 300 to 500 sccm, with the other process parameters being fixed. During deposition, the substrates were fed at a line speed of 0.3 m/min. Table I shows the operating conditions for SiO_x thin-film deposition.

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 determined by X-ray photoelectron spectroscopy (XPS, Thermo Electronics, Multilab ESCA2000) and Fourier transform infrared spectrometry (FTIR, Bruker IFS-66/S). The optical transmittance of the deposited films was examined using ultraviolet-visible spectroscopy (Scinco, UV S-2100). The surface morphology of the thin films was observed by field-emission scanning electron microscopy (Hitachi, S-4700).

Results and Discussion

Figures 2a and b show the effect of HMDS and oxygen flow rates on the deposition rate of silicon oxide in gas mixtures containing Ar/O₂/HMDS (bubbled by Ar flow at 60°C) and at 12 kV of 25 kHz ac power. The oxygen flow rate was maintained at 300 sccm when the HMDS flow rate was varied, and the HMDS flow rate was maintained at 15 sccm when the oxygen flow rate was varied. The sample was a glass substrate, and the substrate was fed to the AP-PECVD system at 0.3 m/min through an in-line process. Ar (2 slpm) was used to activate the atmospheric-pressure plasma. Ar showed better deposition characteristics, such as plasma stability, fewer impurities in the film, etc., than He (not shown). As shown in Fig. 2a, an increase of HMDS flow rate from 8 to 38 sccm increased the film growth rate from 15.1 ± 1.3 to 100.6 ± 12 nm/min. However, when the HMDS flow rate was >30 sccm, a white powderlike material formed on the surface of the deposited film. This was attributed to the increased silicon source in the gas mixture.¹¹ The increase in HMDS flow rate in the gas mixture also increased the possibility of nucleation of the silicon source in the gas phase before it reached the sample surface. Therefore, the white powderlike material formed on the sample surface at >30 sccm HMDS is believed to be due to a homogeneous reaction of SiO₂ in the gas phase.

As shown in Fig. 2b, the deposition rate was increased from 21.8 ± 2.6 to 37.4 ± 0.5 nm/min when the oxygen flow rate was increased from 300 to 450 sccm while keeping the HMDS flow rate at a constant 15 sccm. Further increases in oxygen flow rate to 500 sccm almost saturated the deposition rate. The increase in deposition rate with increasing oxygen flow rate is believed to be related to the increased reaction between HMDS and oxygen. However, no further increase in growth rate was observed when the oxygen flow rate was <450 sccm due to the complete decomposition of HMDS in the gas mixture.¹³

The binding states of the films deposited as a function of the HMDS flow rate and oxygen flow rate in Fig. 2 were measured using FTIR. The results are shown in Fig. 3a and b as a function of

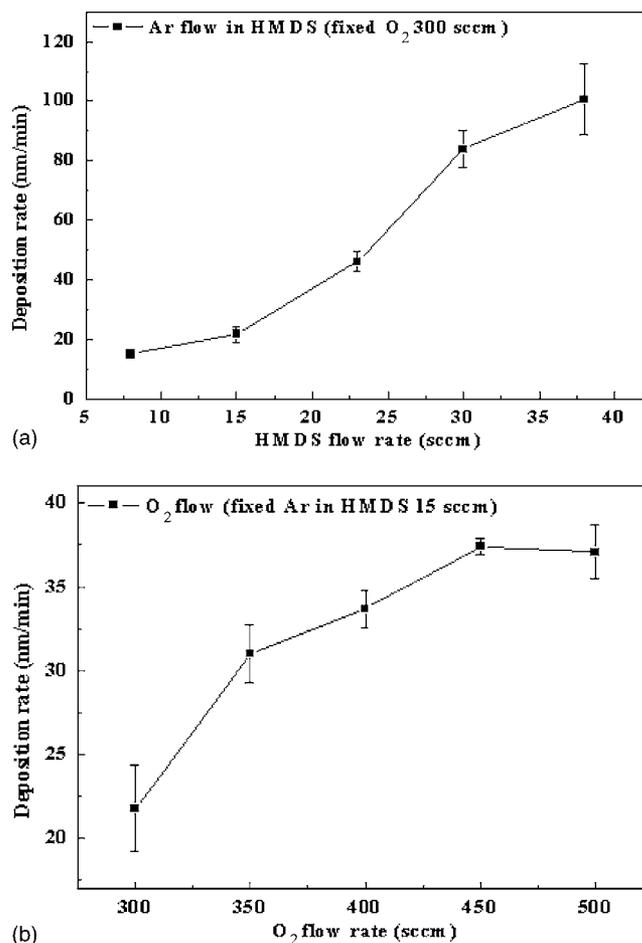


Figure 2. Deposition rate of the SiO_x films as a function of (a) HMDS flow rate and (b) O₂ flow rate using HMDS/O₂/Ar (2 slm) at an applied voltage of 12 kV (25 kHz). When the HMDS flow rate was varied, the oxygen flow rate was maintained at 300 sccm, and when the oxygen flow rate was varied, HMDS flow rate was maintained at 15 sccm.

the HMDS and oxygen flow rates, respectively. The films were deposited on silicon wafers (p-type, <100>) and the thickness was maintained at 200 nm. The bonding peak related to Si–O–Si could be observed at 800–810, 1000–1100,¹¹ and near 1150 cm⁻¹.¹⁴ However, no noticeable peak related to carbon, such as Si–(CH₃)_x located at 1260–1275 cm⁻¹,¹³ could be observed, indicating no significant amount of carbon in the deposited film. Instead, peaks related to Si–OH could be observed at 925–930 and 3350–3650 cm⁻¹.¹⁴ As shown in Fig. 3a, the increase in HMDS flow rate decreased the level of Si–O–Si bonding and increased the proportion of Si–OH bonding. The Si–OH bonding observed in the figure appears to be the result of the incomplete dissociation/oxidation of HMDS due to the high HMDS flow rate.¹¹ Therefore, more incomplete SiO₂ appears to be formed by increasing the HMDS flow rate. When the oxygen flow rate was increased at a fixed HMDS flow rate of 15 sccm, as shown in Fig. 3b, an increase in Si–O–Si bonding could be observed up to 450 sccm, possibly due to the further dissociation and oxidation of HMDS remaining in the gas mixture. However, a further increase in the oxygen flow rate to 500 sccm saturated the Si–O–Si bonding peak, possibly due to the complete dissociation and oxidation of the HMDS remaining in the gas mixture. No significant change in the level of Si–OH could be observed, possibly due to the low sensitivity of the Si–OH bonding peak.

The atomic compositions of the films deposited as a function of

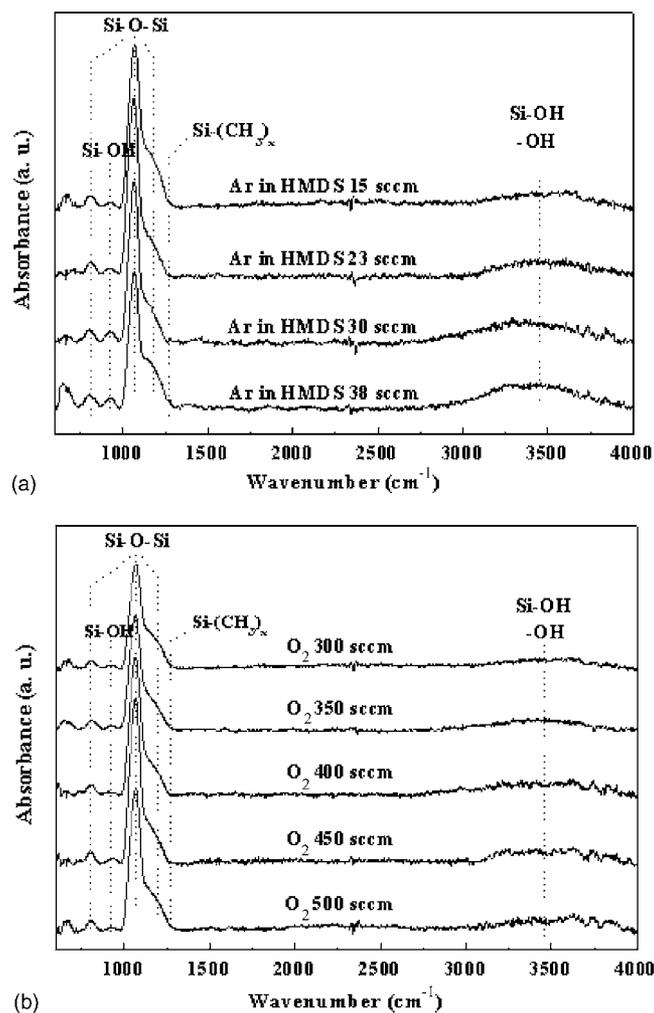


Figure 3. FTIR spectra of the SiO_x deposited at different (a) HMDS flow rates and (b) O_2 -gas flow rates by AP-PECVD. The deposition conditions are the same as those in Fig. 2.

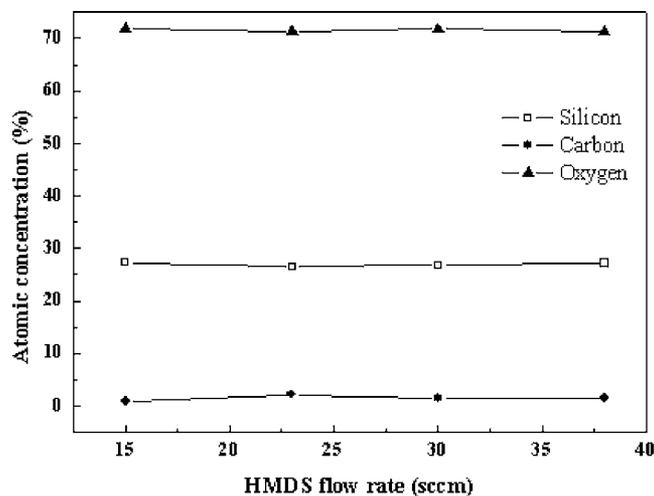


Figure 4. Atomic composition of thin films deposited at different HMDS flow rates measured by XPS. The deposition conditions are the same as those in Fig. 2.

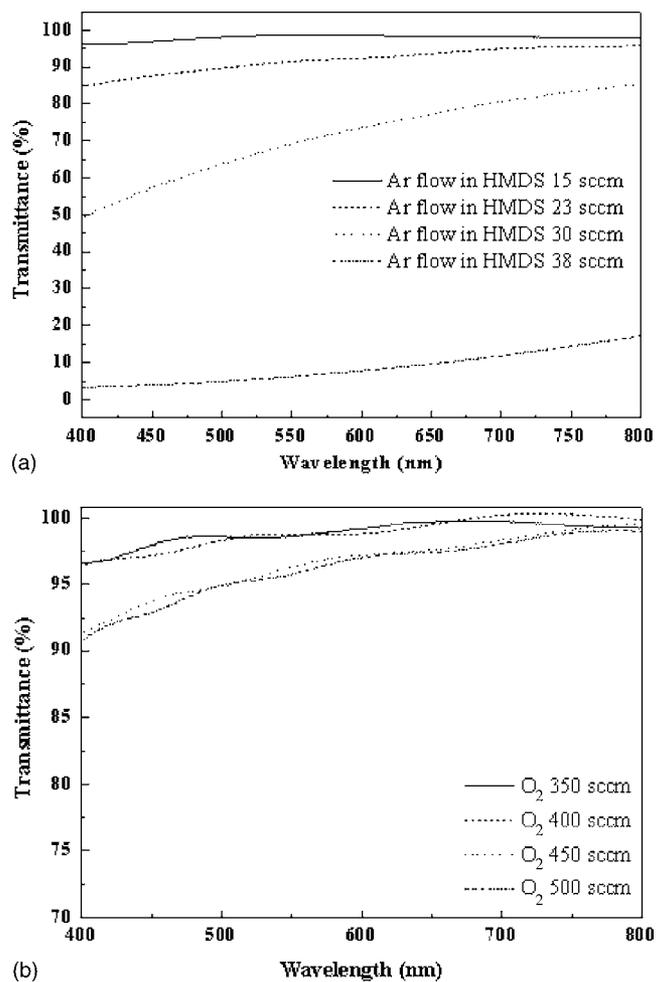


Figure 5. Optical transmittance spectra of the deposited films as a function of (a) HMDS flow rate and (b) oxygen flow rate. The deposition conditions are the same as those in Fig. 2.

the HMDS flow rate in Fig. 2 were measured using XPS, and the results are shown in Fig. 4. Silicon, oxygen, and carbon were observed in the films with no nitrogen. The hydrogen observed by FTIR could not be measured by XPS due to the difficulty in measuring the hydrogen level. As shown in the figure, the percentages of silicon, oxygen, and carbon in the film was approximately 26.9 ± 0.4 , 71.55 ± 0.4 , and $1.5 \pm 0.6\%$, respectively, and no significant change in composition could be observed when the HMDS flow rate was varied from 15 to 38 sccm. When the atomic compositions of the deposited film were measured at different oxygen flow rates (Fig. 2), the percentage of silicon, oxygen, and carbon remained in the range of 27.0 ± 0.2 , 72.12 ± 0.2 , and $0.92 \pm 0.2\%$, respectively, indicating no significant change in composition (data not shown). Therefore, under all conditions investigated, HMDS appears to be mostly dissociated and oxidized by the AP-PECVD. Therefore, a SiO_2 -like film containing hydrogen and a small amount of carbon could be obtained under all conditions examined.¹³

For the films deposited in Fig. 2, the optical transmittance over the wavelength range from 400 to 800 nm was also measured. Figure 5 shows the results as a function of (a) HMDS flow rate and (b) oxygen flow rate. Six hundred nanometer thick films were deposited on glass substrates to measure the optical transmittance. As shown in Fig. 5a, higher optical transmittance was obtained for the lower HMDS flow rate, and the optical transmittance was $>95\%$ when at a HMDS flow rate of 15 sccm. The decrease in optical transmittance with increasing HMDS flow rate was related to light scattering by

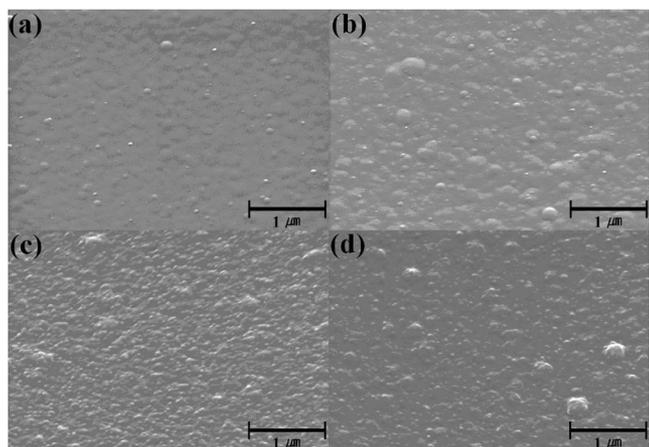


Figure 6. SEM micrographs of the deposited films as a function of the HMDS flow rate: (a) 15, (b) 23, (c) 30, and (d) 38 sccm. The deposition conditions are the same as those in Fig. 2.

the white powderlike material formed on the deposited film. This white powderlike material on the film had not only a higher level of Si–OH bonding but also higher porosity, which decreased the optical transmittance of the film.¹⁵ In the case of the film deposited as a function of the oxygen flow rate, as shown in Fig. 5b, the optical transmittance was also >95% when the oxygen flow rate was <400 sccm. However, further increases in the oxygen flow rate to 500 sccm decreased the optical transmittance slightly. The decrease in optical transmittance was related to the increase in surface roughness with increasing oxygen flow rate.

The surface morphology of the films shown in Fig. 2 was observed by scanning electron microscopy (SEM). Figures 6 and 7 show the morphology at different HMDS flow rates and oxygen flow rates, respectively. Films 300 nm thick deposited on the glass substrate were used as the samples. As shown in Fig. 6, the increase in HMDS flow rate increased the surface roughness and number of particles on the surface, possibly due to the formation of white powderlike material in the film. In addition, when the deposited films were scratched with tweezers, an increase in hardness could be observed with decreasing HMDS flow rate, possibly due to the increase in film density and removal of Si–OH from the film. An increase in surface roughness was also observed when the oxygen flow rate was increased, as shown in Fig. 7. The increase in surface roughness with increasing oxygen flow rate was attributed to the formation of silicon-oxide particles in the gas phase during precursor decomposition. This was attributed to the higher level of oxygen in the gas mixture as a result of inserting both gases through the same gas-injection holes. A method, such as the separation of gas-injection holes, is needed to improve the surface morphology at high oxygen-gas flow rates. Although the increase in oxygen flow rate did not improve the properties of the films deposited, a smooth SiO₂-like film could be obtained using a pin-to-plate AP-PECVD system at temperatures <50°C with an optimum mixture of HMDS and oxygen in Ar, which might be applicable as a thin-film diffusion barrier.

Conclusion

SiO₂-like thin films were deposited by AP-PECVD using a pin-to-plate DBD with HMDS/O₂/Ar as a function of the HMDS flow rate and oxygen flow rate at temperature <50°C, and the characteristics of the deposited film were investigated. An increase in HMDS flow rate and oxygen flow rate in a gas mixture of HMDS (bubbled through Ar flow at 60°C) /O₂/Ar (2 slm) not only decreased the optical transmittance but also increased the surface roughness as a result of homogeneous nucleation in the gas phase. At higher HMDS flow rates, a white powderlike material formed in the film due to the

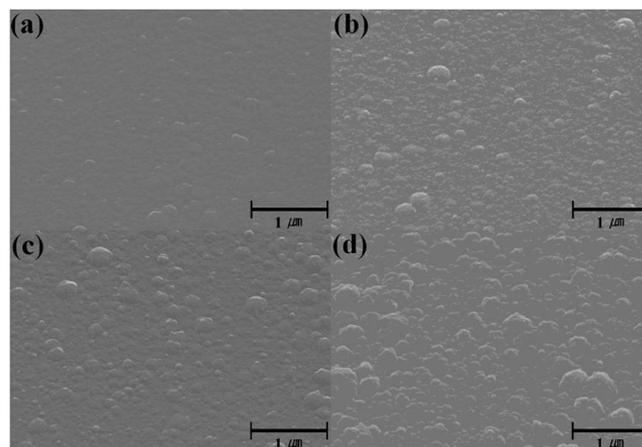


Figure 7. SEM micrographs of the deposited films as a function of the oxygen flow rate: (a) 350, (b) 400, (c) 450, and (d) 500 sccm. The deposition conditions are the same as those in Fig. 2.

increased reaction of the silicon source (HMDS) in the gas mixture. In addition, the surface roughness was increased at a higher oxygen flow rate, which was attributed to small SiO₂ particles formed in the gas phase. The increased white powderlike material obtained at the high HMDS flow rate showed increased Si–OH bonding and porosity in the film and decreased hardness. The change in HMDS flow rate (15–38 sccm at 300 sccm O₂) or oxygen flow rate (300–500 sccm at 15 sccm HMDS) did not alter the composition of the deposited material significantly, and a SiO₂-like thin film with hydrogen and a small amount of carbon in the film could be obtained for all samples. By using an optimum gas mixture of HMDS (15 sccm)/O₂ (300 sccm)/Ar (2 slm), a smooth, hard, and optically transparent thin film similar to the SiO₂ deposited by low-pressure PECVD could be obtained by AP-PECVD at a deposition rate of approximately 21 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.*, **174–175**, 1043 (2003).
4. K. L. Choy, *Prog. Mater. Sci.*, **48**, 57 (2003).
5. H. O. Pierson, *Handbook of Chemical Vapor Deposition Principles, Technology and Applications*, William Andrew Publishing, Noyes, New York (1999).
6. M. A. Liberman and A. J. Lichtenberg, *Principles of Plasma Discharges and Materials Processing*, Wiley Interscience, New York (1994).
7. 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).
8. L. J. Ward, W. C. E. Schofield, J. P. S. Badyal, A. J. Goodwin, and P. J. Merlin, *Chem. Mater.*, **15**, 1466 (2003).
9. S. Martin, F. Massines, N. Gherardi, and C. Jimenez, *Surf. Coat. Technol.*, **177–178**, 693 (2004).
10. D. Vangeneugden, S. Paulussen, O. Goossens, R. Rego, and K. Rose, *Chem. Vap. Deposition*, **11**, 491 (2005).
11. 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).
12. Y. H. Lee, S. J. Kyung, C. H. Jeong, and G. Y. Yeom, *Jpn. J. Appl. Phys., Part 2*, **44**, L78 (2005).
13. X. Zhu, F. Arefi-Khonsari, C. Petit-Etienne, and M. Tatoulian, *Plasma Processes Polym.*, **2**, 407 (2005).
14. F. Massines, N. Gherardi, A. Fornelli, and S. Martin, *Surf. Coat. Technol.*, **200**, 1855 (2005).
15. T. Gunji, Y. Makabe, N. Takamura, and Y. Abe, *Appl. Organomet. Chem.*, **15**, 683 (2001).