Journal of the Korean Physical Society, Vol. 66, No. 9, May 2015, pp. 1410∼1415

Improving the Gas Barrier and Mechanical Properties of a-SiO_x Films Synthesized at Low Temperature By Using High Energy and Hydrogen Flow Rate Control

Su B. Jin, Wen Long, B. B. Sahu and Jeon G. Han*
NU-SKKU Joint Institute for Plasma-Nano Materials,
Center for Advanced Plasma Surface Technology,
Sungkyunkwan University, Suwon 440-746, Korea

M. Hori
NU-SKKU Joint Institute for Plasma-Nano Materials, Plasma Nanotechnology Research Center,
Nagoya University, Furu-cho, Chikusa-ku, Nagoya 464-8603, Japan

(Received 29 October 2014, in final form 24 November 2014)

Silicon-oxide thin films were deposited on polyethylene-terephthalate (PET) and glass substrates for applications in transparent barrier packaging and replacement display cover glasses by using plasma-enhanced chemical vapor deposition (PECVD). The bias conditions and the input power in the radio-frequency plasma were changed to optimize the gas barrier and the mechanical properties of the silicon-oxide thin film. We made an advanced plasma source for large-area PECVD (370 × 470 mm^2 size). The dissociation of the octamethylycyclodisiloxane (OMCTS) precursor was controlled by using the plasma processing parameters. The gas barrier and the mechanical properties of the a-SiO_x film were improved by controlling the plasma process parameters. The gas barrier and the mechanical properties of the coatings were examined using a Permatran (MOCON) system and a pencil hardness measurement. The chemical structure properties of the coatings were examined by using Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS). The properties of the a-SiO_x thin films were improved by the dissociation of OMCTS obtained by using various appropriate plasma processing parameters.

PACS numbers: 66.90.+r, 62.20.-x
Keywords: a-SiO_x, Gas barrier property, Mechanical property, Low-temperature process
DOI: 10.3938/jkps.66.1410

I. INTRODUCTION

Silicon-oxide thin films are transparent protective coatings with anti-scratch, chemical resistance, and barrier properties that have recently emerged as prime coatings for a range of functional optical coatings on polymer substrates in mobile electronics, digital cameras and other digital applications [1, 2]. Many optically-transparent, protective coating materials, as well as low-temperature plasma processes, have been developed for these applications. The unique properties of a-SiO_x films make them applicable as inter-metal dielectrics, gas barriers and protective coatings [3–5]. In addition, large-scale silicon-oxide film coatings on polymers are increasingly being used for various applications. The use of conventional chemical-vapor deposition (CVD) coating methods is common. However, these coating methods have been well-documented and are being extensively utilized in both academic and industrial fields. These conventional coating methods have disadvantages regarding substrate heat damage. The high processing temperatures of these methods are unsuitable for articles made of heat-sensitive materials such as polymers. Improvements in the gas barrier and the mechanical properties of the films produced, as well as leaving the substrates free of thermal damage, are key factors that can be controlled by using a plasma process and a low-temperature plasma-enhanced chemical-vapor deposition (PECVD) system.

A coating technique for producing a gas barrier with a denser structure and hardness by controlling the RF bias and the hydrogen flow rate is reported. The coating layer deposited by using low-temperature plasma processes was electronically meta-stable because the process temperature was very low, and the substrate temperature was always less than 100 °C for the formation of a thermodynamically-stable structure with stoichiomet-

*E-mail: hanjg@skku.edu; Fax: +82-31-290-5665

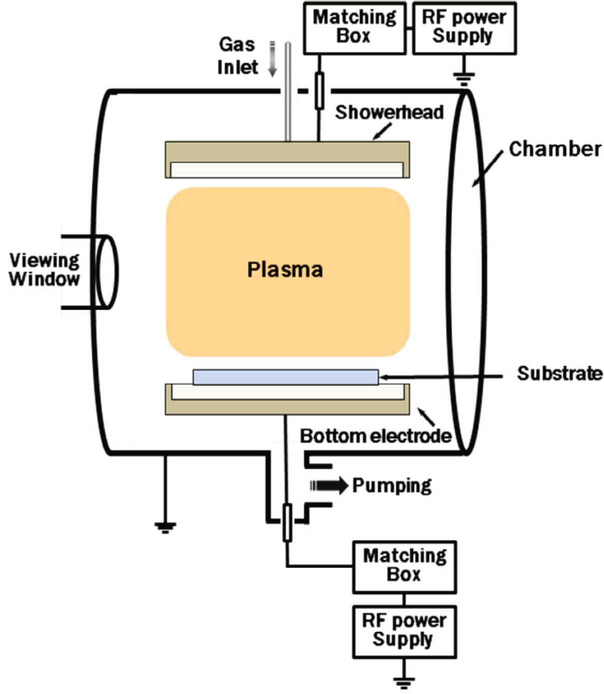

Fig. 1. (Color online) Schematic diagram of the large-area PECVD process and RF power and RF power apparatus used to deposit the SiO_x film.

ric electronic bonding that could prevent deterioration of the polymer substrate. We report on the relationship between the plasma's parameters and the film's properties in terms of the plasma process parameters.

II. EXPERIMENTAL PROCEDURE

A step profilometer (KLA Tencor Alpha-step IQ) was used to measure and adjust the film's thickness. Attenuated total reflection Fourier-transform infrared absorption (ATR FT-IR) microscopy provided spatially-resolved information about the qualitative chemical binding composition over the footprint area. The spectra were obtained at wavenumbers between 2000 and 400 cm^{-1} at a spectral resolution of 4 μm by using an ATR germanium crystal. The number of scans was 64. A polynomial baseline correction was applied to all ATR transmittance spectra. The ratio of Si/O/C in the deposited a-SiO_x thin films was also examined by using X-ray photoelectron spectroscopy (XPS, VG Multilab 2000) with a Mg/Al twin X-ray source. The anode voltage and current were 15 kV and 20 mA, respectively, and the background pressure in the analytical chamber was approximately 1.0×10^{-7} Torr. The size of the X-ray spot was 10 × 10 mm^2, and the take-off angle of the photoelectrons was 90° with respect to the sample's surface. The substrate temperature was monitored by using a K-type thermocouple fixed near the surface of the substrate electrode. The surface hardness of the a-SiO_x film was measured by using a pencil hardness test according to the standard ASTM D3363 method. The barrier properties of the films were tested over 24 hours by analyzing the water vapor transmission rate (WVTR). The WVTRs were measured under similar conditions at temperatures from 24 to 38 °C by using a Permatran (MOCON) system. Using the standard protocol, we measured the hardness at 10% of the film thickness, and the modulus was taken at 100 nm. Pencils with hardness's ranging from B to 9H were used to scratch the surfaces of various substrates at an angle of 45°.

Table 1. Deposition parameters

Parameter	Condition
Base pressure	$< 2.0 \times 10^{-3}$ Torr
Deposition pressure	6.5×10^{-2} Torr
Top electrode (RF, 13.56 MHz)	300 W
Bottom electrode (RF, 13.56 MHz)	350 ∼ 450 W
O_2 flow rate	60 sccm
H_2 flow rate	0 ∼ 20 sccm
Film thickness	100 nm
Temperature	Room temperature
Substrates	Polyethylene-terephthalate (PET) and Glass

III. RESULTS AND DISCUSSION

The rates of deposition of the a-SiO_x film on the polyethylene-terephthalate (PET) and the glass substrates coated for 5 min were determined. The deposition rate as a function of the RF power and bias was measured by using an alpha step profiler. We observed similar deposition rates by increasing the RF power on the bottom electrode at a deposition pressure of 6.5×10^{-2} Torr. Figure 2(a) shows that the rate of a-SiO_x film deposition increased with increasing RF power from 350 W to 450 W. The higher input RF power of 400 W produced a stress-free film with good adhesion at a high deposition rate. The increasing ion density was attributed to an increase in the electron density, which led to the formation of reactive ions from the dissociation of the precursor [6–8]. In addition, we determined the effect of hydrogen flow (Fig. 2(b)). The rate of a-SiO_x film deposition was decreased by increasing the hydrogen flow rate. However, we think that a large-size electrode with suitable plasma processes might have an improved gas barrier and improved mechanical properties.

Figures 3(a) and (b) show the FT-IR spectra at wavenumbers from 2000 to 400 cm^{-1} for the a-SiO_x films deposited on the Si wafers (100) with an increasing RF

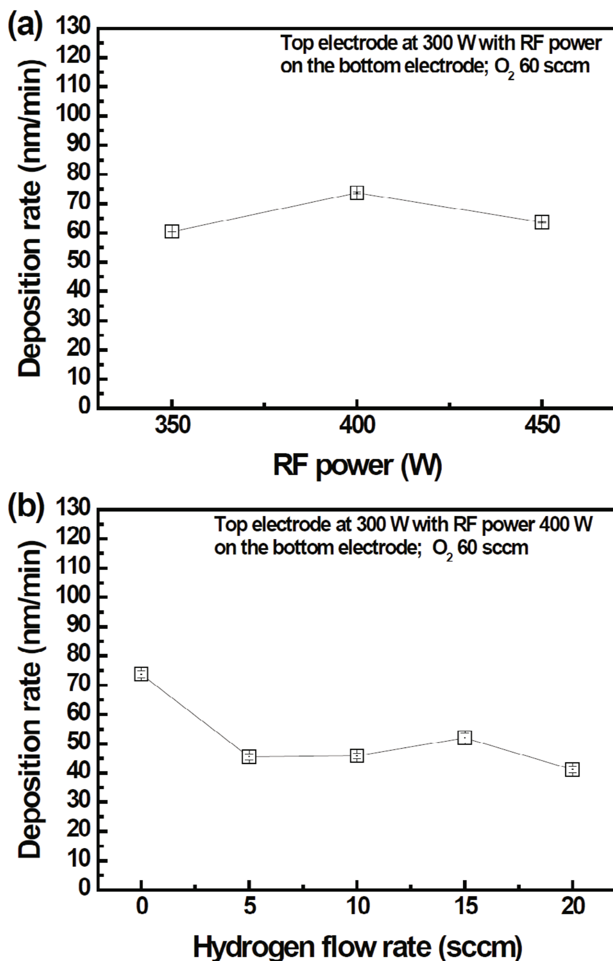

Fig. 2. Deposition rates of the films deposited with (a) increasing RF power on the bottom electrode with the top electrode at 300 W and with (b) increasing hydrogen flow rate.

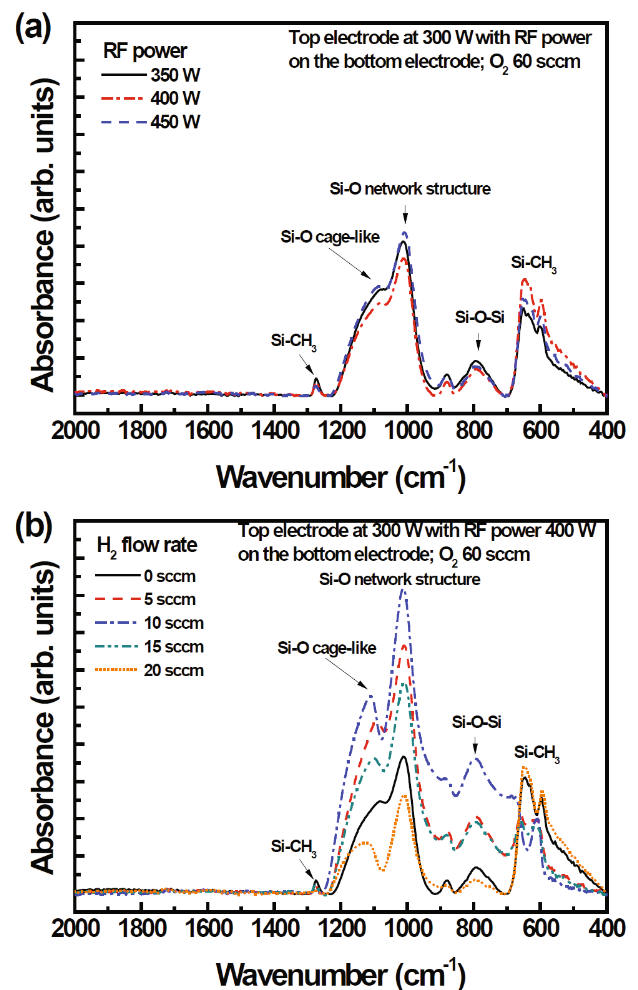

Fig. 3. (Color online) FT-IR spectra of the SiO_x film deposited with increasing RF power and H_2 gas. (a) FT-IR spectra showing the chemical structure of the SiO_x films measured with the top electrode at 300 W and an RF power at the bottom electrode. (b) FT-IR spectra showing the chemical structure of the SiO_x films measured at different H_2 flow rates.

power to bottom electrode with the top electrode at 300 W and an increasing hydrogen flow rate, respectively. The intensities of the peaks for the Si-CH_3, the Si-O-Si, Si-O cage-like and the Si-O network structures were affected by the RF power and the hydrogen flow rate. The SiO_x film showed main peaks for the Si-O network and the Si-O-Si structures. The absorption band at 800 cm^{-1} was assigned to the Si-O-Si stretching vibrations [9, 10]. The Si-O network structure increased with increasing RF power from 350 W to 450 W (Fig. 3(a)). In addition, Fig. 3(b) shows that the intensities of the Si-O network structure and the Si-O-Si stretching vibration increased and the intensity of the Si-CH_3 structure decreased with increasing hydrogen flow rate from 0 sccm to 20 sccm. For a-SiO_x films deposited at a hydrogen flow rate of 10 sccm, the Si-O network structure and the Si-O-Si chemical structure were characterized by using the high-intensity peaks. Thus, the a-SiO_x thin film was considered to have an increasing film density for a suitable hydrogen flow rate. Overall, we know that a high input energy improves the mechanical properties and the deposition rate of the a-SiO_x films [11,12].

The XPS results were in good agreement with those obtained from the FT-IR analysis. Figures 4(a) and (b) show the changes in the atomic compositions of the deposited a-SiO_x films as functions of the RF power and the hydrogen flow rate. The C/Si atomic ratio was $<$ 0.7 when the RF power was $>$ 350 W, where the carbon in the deposited film is believed to exist in a highly cross-linked state. The O/Si atomic ratio in the a-SiO_x film began to increase as the RF power was increased to 400 W with a corresponding decrease in the carbon content in the a-SiO_x film. In addition, the chemistry of the a-SiO_x film changed from a carbon chemistry to an oxygen chemistry with increasing hydrogen flow rate. The atomic compositions of the deposited a-SiO_x films

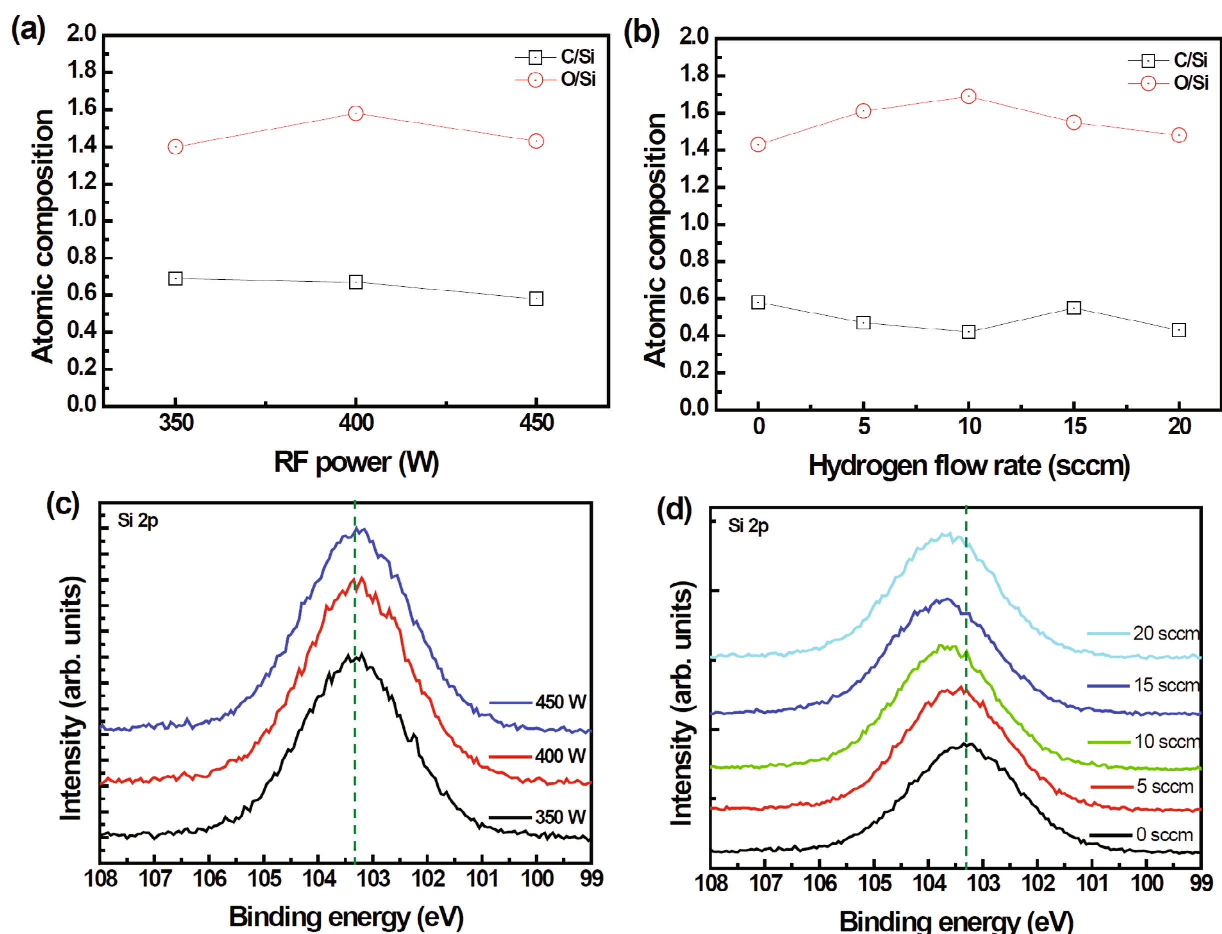

Fig. 4. (Color online) (a) Change in the atomic compositions of the SiO_x films deposited with increasing RF power. (b) Change in the atomic compositions of the SiO_x films deposited with increasing the hydrogen flow rate. XPS binding energy for the Si 2p peaks of the SiO_x films deposited with increasing (c) RF power and (d) hydrogen flow rate.

were characterized by using low C/Si and high O/Si ratios for an input gas flow rate of H_2 of 10 sccm. Figure 4(c) and (d) show the Si 2p spectra with increasing RF power and hydrogen flow rate. Figure 4(c) shows the same binding energy with increasing RF power. However, Fig. 4(d) shows a shift in the Si 2p peak from 103.3 eV to 103.7 eV [13]. This can be explained by the chemical structure of a-SiO_x having changed from a SiO_3 to a SiO_4 chemical structure. In other words, the density of the a-SiO_x film improved. We observed a high intensity of the Si-O-Si chemical structure in the FT-IR analysis. The atomic compositions of the deposited a-SiO_x films were characterized by using the low C/Si and the high O/Si ratios for an input RF power of 400 W. The atomic compositions of the deposited a-SiO_x films were characterized by using the low C/Si and the high O/Si ratios at an input gas flow rate of H_2 of 10 sccm. Consequently, we controlled the chemical structure of the a-SiO_x film by using suitable plasma parameters and obtained good properties.

Figures 5(a) and (b) show the changes in the substrate temperature observed by using a thermometer. Figure 5(a) shows that the substrate temperature increased with increasing RF power. In addition, the substrate temperature increased with increasing hydrogen flow rate (Fig. 5(b)). The enhanced kinetic energy of the ionized particles was transferred to the substrate by electrons overcoming the negative floating potential and ions being accelerated in the sheath [6–8,11]. The impact energies transfer to the substrate, which can result in substrate heating. However, a-SiO_x thin-film deposition can be performed at low temperatures (< 100 °C).

Figures 6(a) and (b) show that the pencil hardness of the a-SiO_x films increased with increasing input energy (RF power) and increasing hydrogen flow. For a-SiO_x films deposited on glass substrates at an RF power of 400 W with an RF power of 300 W on the top electrode at room temperature, the surface hardness of the glass substrate was measured as 8H (Fig. 6(a)). In addition, a decreasing pencil hardness was observed with increasing hydrogen flow rate. However, the surface of the a-SiO_x film had a high pencil hardness with a highly dense film at a hydrogen flow rate of 10 sccm (Fig. 6(b)).

Figures 7(a) and (b) show the WVTR value for a-

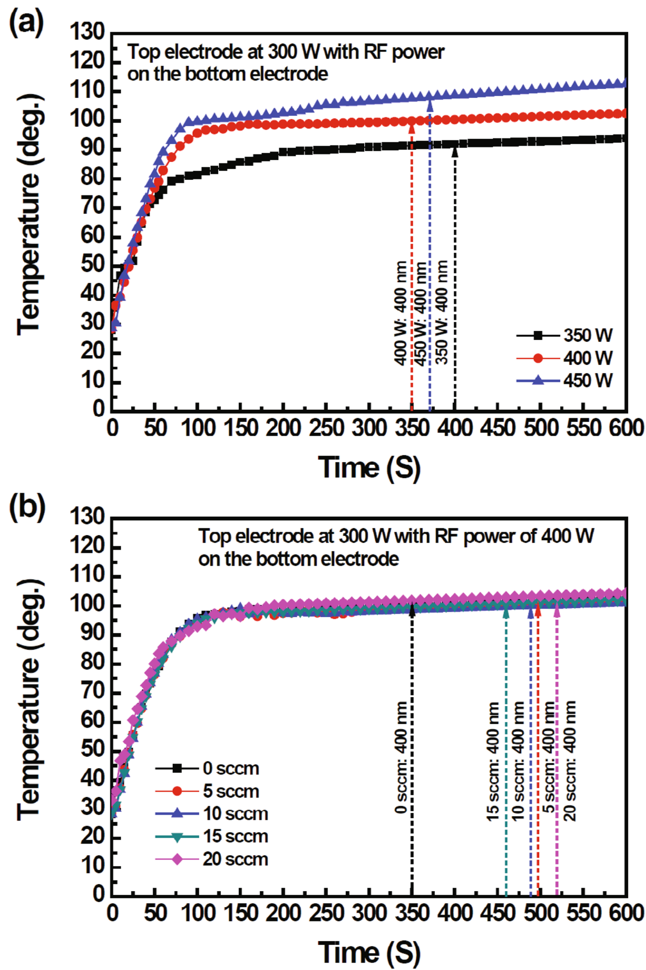

Fig. 5. (Color online) Substrate temperature for increasing (a) RF power and (b) hydrogen flow rate measured by using a thermometer.

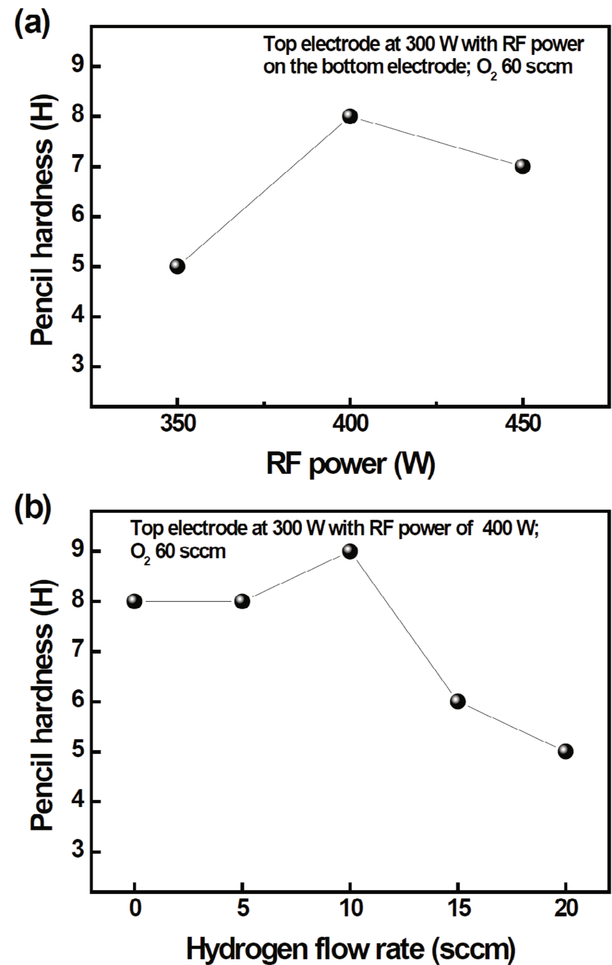

Fig. 6. (a) and (b) Mechanical properties of the SiO_x film deposited by using various values of the RF power and the hydrogen flow rate.

SiO_x films coated on polyethylene terephthalate (PET) substrates as functions of the input RF power and the hydrogen flow rate. Figure 7(a) shows that the WVTR of the a-SiO_x films deposited was lowest (0.98 g/m^2/day) for a 300 W input RF power to the top electrode, a 400 W RF power to the bottom electrode, and an input O_2 gas flow rate of 60 sccm. Figure 7(b) shows the WVTR of the a-SiO_x thin films coated on PET substrates as functions of the H_2 flow rate from 0 to 20 sccm with an input top electrode power of 300 W, a RF power of 400 W to the bottom electrode and an O_2 flow rate of 60 sccm. We observed that the WVTR of the a-SiO_x films decreased with increasing hydrogen flow rate. The WVTR of the deposited a-SiO_x films was lowest (0.32 g/m^2/day) for an input H_2 gas flow rate of 10 sccm. Consequently, the stronger Si-O-Si and Si-O network structure chemistry of a-SiO_x films improves the barrier properties (WVTR) for suitable value of the RF power and the hydrogen flow rate. The nano and macro defects in the a-SiO_x film were reduced by controlling the plasma process.

IV. CONCLUSION

a-SiO_x films were deposited on polyethylene-terephthalate (PET) and glass substrates at temperatures less than 100 °C by using a large-area PECVD system. The dissociation of the octamethylcyclotetrasiloxane (OMCTS) precursor was controlled by using the plasma processing parameters. The SiO_x thin film was successfully synthesized without any damage to the polymer at a low temperature. Various radical compositions were observed to be important control factors for determining the chemical structural properties of the a-SiO_x films. A higher energy and a higher ion flux affect the Si-O-Si bonds and Si-O network structure bonds, and bring about high pencil hardness and good gas barrier properties. As a result, the pencil hardness of the a-SiO_x film was found to be 8H (glass substrate) and 2H (PET substrate). In addition, the WVTR of the a-SiO_x films deposited was lowest at 0.32 g/m^2/day.

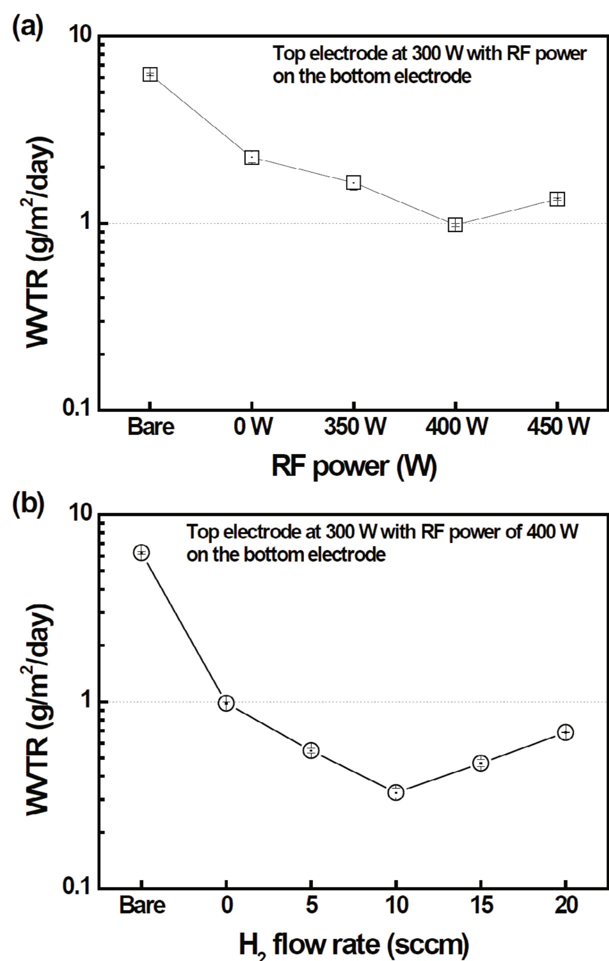

Fig. 7. WVTR of SiO$_x$ films as functions of (a) the RF power to the top electrode and (b) the hydrogen flow rate. (The thicknesses of all films were 400 nm.)

ACKNOWLEDGMENTS

This study was supported by the R&D Program of 'Plasma Advanced Technology for Agriculture and Food (Plasma Farming)' through the National Fusion Research Institute of Korea (NFRI) funded by the Government, by the Global Research Development Center (GRDC), a program of the Ministry of Science, ICT and Future Planning (MSIP, Grant No. 20120006672, 2nd stage, 1st year) and by the Korea Institute for Advancement of Technology (KIAT), which is funded by the Ministry of Trade, Industry & Energy (MOTIE, Grant No. N0000590).

REFERENCES

[1] N. Tomozeiu, E. E. van Faassen, W. M. Arnoldbik, A. M. Vredenberg and F. H. P. M. Habraken, Thin Solid Films **382**, 420 (2002).
[2] Y. Sawada, S. Orgawa and M. Kogoma, J. Phys. D: Appl. Phys. **1661**, 28 (1995).
[3] G. R. Nowling, M. Yajima, S. E. Babayan, M. Moravej, X. Yang, W. Hoffman and R. F. Hicks, Plasma Sources Sci. Technol. **447**, 14 (2005).
[4] K. Teshima, Y. Inoue, H. Sugimura and O. Takai, Surf. Coat. Technol. **583**, 169 (2003).
[5] S. E. Babayan, J. Y. Jeong, A. Schutze, V. J. Tu, M. Moravej, G. S. Selwyn and R. F. Hicks, Plasma Sources Sci. Technol. **573**, 10 (2001).
[6] Su B. Jin, Yoon S. Choi, In S. Choi and Jeon G. Han, Thin Solid Films **6763**, 519 (2011).
[7] Su B. Jin, Joon S. Lee, Yoon S. Choi, In S. Choi and Jeon G. Han, Thin Solid Films **6334**, 519 (2011).
[8] Su B. Jin, Yoon S. Choi, Youn J. Kim, In S. Choi and Jeon G. Han, Surf. Coat. Technol. **S139**, 205 (2010).
[9] C. Y. Wang, Z. X. Shen and J. Z. Zheng, Appl. Spectrosc. **1347**, 55 (2001).
[10] G. Socrates, *Infrared Characteristic Group Frequencies*, 2nd ed. (Wiley, Chichester, UK).
[11] Su B. Jin, Youn J. Kim, Yoon S. Choi, In S. Choi and Jeon G. Han, Thin Solid Films **6385**, 518 (2010).
[12] Su B. Jin, Sung I. Kim, Yoon S. Choi, In S. Choi and Jeon G. Han, Curr. Appl. Phys. **1107**, 11 (2011).
[13] L. M. Han, J.-S. Pan, S.-M. Chen and N. J. Electrochem. Soc. **148**, 148 (2001).