

Characteristics of SiO_x Thin Films Deposited by Using Direct-Type Pin-to-Plate Dielectric Barrier Discharge with PDMS/He/O₂ Gases at Low Temperature

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SiO₂-like thin films were deposited at low temperatures (<70 °C) by using an atmospheric pressure plasma enhanced chemical vapor deposition (AP-PECVD) with a pin-to-plate-type dielectric barrier discharge (DBD) and a gas mixture containing polydimethylsiloxane (PDMS), bubbled by He/O₂. The films characteristics were investigated as a function of the applied voltage to the power electrode. As the voltage to the power electrode was varied, due to the differences in the dissociation rates of oxygen and PDMS by the plasma, different physical and chemical characteristics of the SiO_x thin film could be obtained. When the applied voltage was lower than 5 kV, the SiO_x thin film with higher carbon and higher Si-OH was observed, possibly due to the lower dissociation rate of PDMS compared to that of oxygen. However, when the applied voltage was higher than 5 kV, a SiO_x thin film with higher Si-CH and with a rough surface was observed due to the higher dissociation rate of PDMS compared to that of oxygen dissociation. At an optimized applied voltage (5 kV), a smooth and stoichiometric SiO₂-like thin film with a low carbon content (1.5 %) was deposited at deposition rate of 12 nm/min.

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I. INTRODUCTION

Recently, there has been increased interest in and development of plasma processes at atmospheric pressure [1, 2]. Operating at reduced pressure requires vacuum chambers with load locks and robotic assemblies to shuttle materials in and out of vacuum. Consequently, the size of the objects that can be treated is limited by the size of the vacuum system.

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. Moreover, they allow for continuous in-line processing of materials. However, no credible AP-PECVD system has yet reached the market.

The deposition of SiO₂ thin films at low substrate temperatures is attracting increasing attention for its potential applications in areas such as organic thin-film transistors (OTFTs) and organic light-emitting diodes (OLEDs), as thin-film water-permeation barrier materials in the next generation flat-panel-display (FPD) devices [3, 4] and as dielectric materials for insulation,

device passivation, etc. in solid-state electronic and optoelectronic devices on plastic substrates [5, 6]. AP-PECVD has been used for the low-temperature deposition of SiO₂ thin films on thermally sensitive materials due to the difficulty of depositing SiO₂ thin films on organic materials at high temperatures.

AP-PECVD of SiO₂ at low temperatures involves the dissociation of volatile silicon precursors/oxygen with plasma and the formation of SiO₂ on the substrate surface [7]. Among the various organo-silicon precursors, polydimethylsiloxane (PDMS) is known to exhibit superior material properties, such as fewer particle problems, compared to other precursors, possibly due to the lower chemical reactivity of PDMS during the deposition using a typical dielectric-barrier-discharge (DBD)-type AP-PECVD [8, 9].

In this study, SiO₂ thin films were deposited at low temperatures by using a modified DBD, called a "pin-to-plate-type DBD," for the generation of a high-density plasma and using a gas mixture of PDMS/He/O₂. Especially, the characteristics of the deposited films were investigated as a function of the applied voltage to the power electrode. 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

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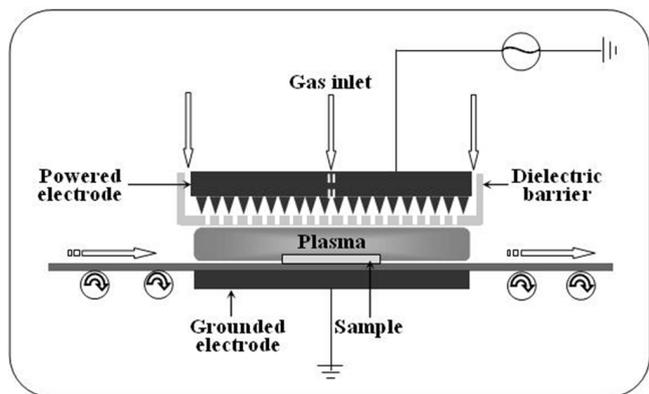


Fig. 1. diagram of the AP-PECVD in-line system (pin-to-plate DBD-type).

applied voltage due to the high electric field at the multiple pins of the power electrode [10].

II. EXPERIMENTS

Figure 1 shows the AP-PECVD in-line system used to deposit the SiO_x films at temperatures lower than 70°C . The discharge system consisted of a multi-pin top-powered electrode and a flat ground electrode separated by approximately 8 mm, with both electrodes covered with an insulating ceramic plate. The size of the electrode was 198 mm length \times 105 mm width. Atmospheric pressure plasma discharges were generated by applying an AC voltage at a frequency of 25 kHz to the multi-pin electrode. The process gas was fed into the system through the shower slits in the ceramic material of the power electrode. The substrate was fed to the AP-PECVD system at 0.3 m/min through an in-line feeder. PDMS pre-polymer and a curing agent (Sylgard 184, Dow Corning, $-\text{OSi}(\text{CH}_3)_2\text{O}-$) were used as the Si precursors. The PDMS composed of a pre-polymer and a curing agent (pre-polymer : curing agent = 10 : 1) was fed into the system by bubbling He gas through the PDMS liquid reservoir kept at room temperature.

The SiO_x thin films were deposited on glass substrates or silicon substrates and the characteristics of the thin film deposited on the substrates were investigated by varying of the voltage applied to the power electrode from 4 kV to 8 kV while the gas composition was fixed at PDMS/He (9 slm) + O_2 (1 slm). During the deposition, the change in the substrate temperature was measured using a thermocouple attached to the glass substrate. 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 using X-ray photoelectron spectroscopy (XPS, Thermo Electronics, Multilab ESCA2000) and Fourier transform infrared spectrometry (FTIR, Bruker IFS-66/S). The surface morphology of the thin films was observed using

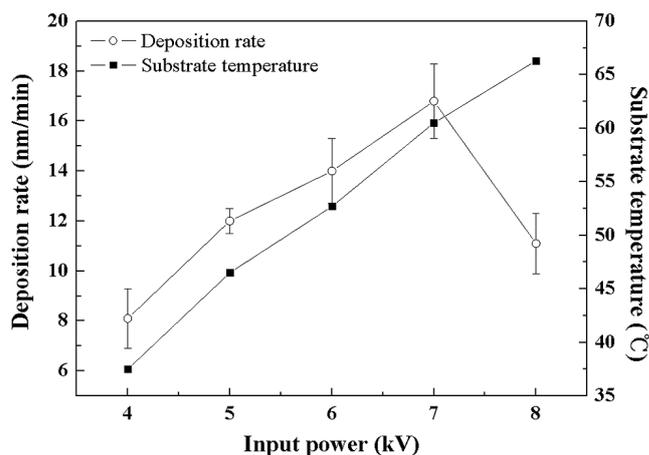


Fig. 2. Deposition rate of SiO_x and substrate temperature as functions of the applied voltage (AC power (25 kHz)) to the power electrode while the reactive gas flow rates were maintained at PDMS/He 9 slm and O_2 1 slm.

field emission scanning electron microscopy (FE-SEM, Hitachi, S-4700).

III. RESULTS AND DISCUSSION

Figure 2 shows the deposition rate of SiO_x measured as a function of the voltage (AC power (25 kHz)) applied to the power electrode while the reactive gas flow rates were maintained at PDMS/He (9 slm) and O_2 (1 slm). Even though the temperature of the ground electrode was kept at room temperature by using a chiller, during the operation of the plasma, the temperature of the substrate could be increased. Therefore, the surface temperature of the glass substrate was measured using a thermocouple as a function of applied voltage after 10 min operation of the plasma and the result is also shown in Figure 2. As shown in the figure, as the applied voltage was increased from 4 kV to 7 kV, the deposition rate was increased from 8.1 ± 1.2 nm/min to 16.8 ± 1.5 nm/min; however, a further increase in the applied voltage to 8 kV decreased the deposition rate to 11.1 ± 1.2 nm/min. In the case of the surface temperature of the substrate, as the voltage applied to the power electrode was increased from 4 kV to 8 kV, the surface temperature was continuously increased from 37.5°C to 66.3°C . Therefore, the SiO_x deposition was obtained at a temperature lower than 70°C . The increase in the SiO_x deposition rate with increasing applied voltage from 4 kV to 7 kV is believed to be related to the increased dissociation rate of PDMS due to the increasing plasma density and to the increased chemical reactions on the substrate could by the increase in the substrate temperature with increasing applied voltage. However, the decrease in the SiO_x deposition rate at an applied voltage of 8 kV appears to be related to the formation of a filamentary discharge,

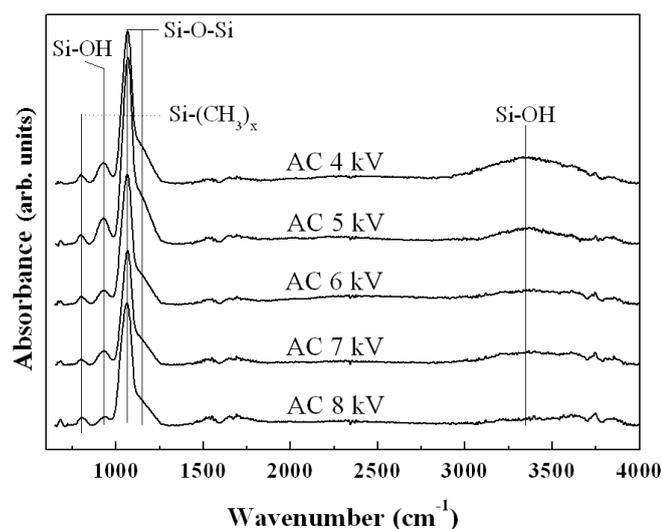


Fig. 3. FT-IR spectra of SiO_x deposited at different applied voltages by the using AP-PECVD. The deposition conditions are the same as those shown in Figure 2.

which is observed at the high applied voltages, in general.

Figure 3 shows the FTIR spectra of the SiO_x thin films deposited on silicon substrates as a function of voltage applied to the power electrode. The deposition conditions were the same as there in Figure 2. The deposition thicknesses of the SiO_x thin films were maintained at 200 nm. An absorption peak related to Si-(CH₃)_x binding was observed at 801 cm⁻¹ [11], absorption peaks related to Si-OH binding were at 925 – 930 and 3350 – 3650 cm⁻¹ [12] and the peaks related to Si-O-Si were observed at 1000 – 1100 and near 1150 cm⁻¹ [12]. As shown in the figure, the peak intensity related to Si-OH decreased with increasing applied voltage while the peak intensity related to Si-(CH₃)_x appears to remain the same. In the case of the peak intensity related to Si-O-Si, the highest peak intensity could be observed at 5 kV. The variation of the binding peaks in SiO_x deposited at varying applied voltages, as observed by FTIR, appears to be related to the differences in the dissociation rates of PDMS and oxygen molecules with increasing applied voltage. Due to the higher binding energy of O-O compared to that of Si-(CH₃)_x, the dissociation rate of the oxygen molecule is less sensitive to the applied voltage than the dissociation rate of PDMS. Therefore, when the applied voltage is high, the PDMS dissociation rate is much higher than the dissociation rate of the oxygen molecule; therefore, the SiO_x deposited can have less oxygen and show a low Si-O-Si binding peak due to the lower dissociation rate of the oxygen molecule. However, when the applied voltage is low, the dissociation rate of the oxygen molecule can be higher than that of PDMS, which can result in an increase in the Si-OH (not Si-O-Si) in the deposited SiO_x, which was formed by abundant oxygen atoms and incompletely dissociated PDMS. However, an

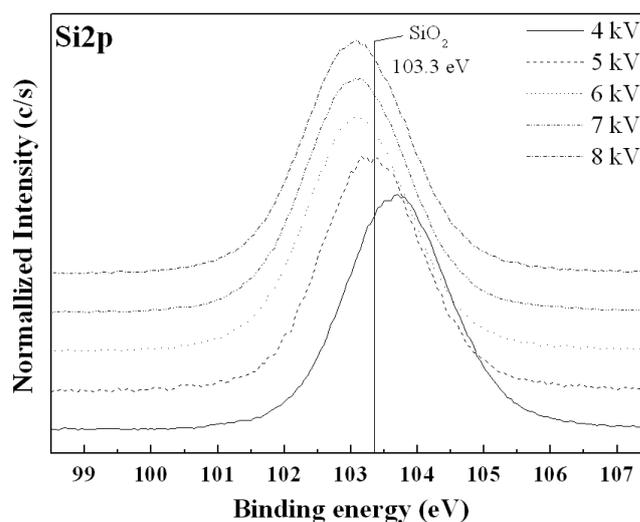


Fig. 4. XPS spectra of Si 2p core levels of SiO_x thin films for various applied voltages. The deposition conditions are the same as those shown in Figure 2.

applied voltage of 5 kV, due to the adequate combination of dissociated oxygen molecules and dissociated PDMS in the deposited thin film, the highest Si-O-Si binding in the deposited thin film appeared to be obtained even though the deposition rate was not the maximum.

Figure 4 shows XPS Si 2p core-level binding energies of SiO_x thin films deposited on glass substrates at varying applied voltages. The deposition conditions were the same as those in Figure 2. As shown in the figure, the Si 2p binding energy was changed from 103.7 eV to 103.1 eV as the applied voltage was changed from 4 kV to 8 kV even though the Si 2p binding energy remained similar for SiO_x deposited at applied voltages from 6 kV to 8 kV. The Si 2p binding energy for SiO₂ is 103.3 eV [13]; therefore, at lower applied voltages, the silicon binding energy is higher than that of SiO₂ and at higher applied voltage, the silicon binding energy is lower than that of SiO₂. The lower Si binding energy for the lower applied voltage is believed to be from abundant Si-OH binding (104.3 eV) [14] in the SiO_x thin film deposited at the lower applied voltage and the higher Si binding energy for the higher applied voltage is believed to be related to the Si-CH binding (not Si-(CH₃)_x due to the more complete dissociation at the high applied voltage) because Si binding energies related to Si-CH_x show lower binding energies compared to that of SiO₂. At 5 kV, the Si 2p binding energy was 103.28 eV; therefore, a Si 2p binding energy close to that of SiO₂ could be obtained [13]. Also, when the carbon percentages in the deposited SiO_x thin films were estimated by using XPS, the lowest carbon percentage, about 1.5 %, could be obtained for the SiO_x deposited at 5 kV and when the atomic composition ratio of Si:O was measured, 1 : 2.2, which is close to the 1 : 2 of SiO₂, could be observed for the SiO_x thin film deposited at 5 kV (not shown).

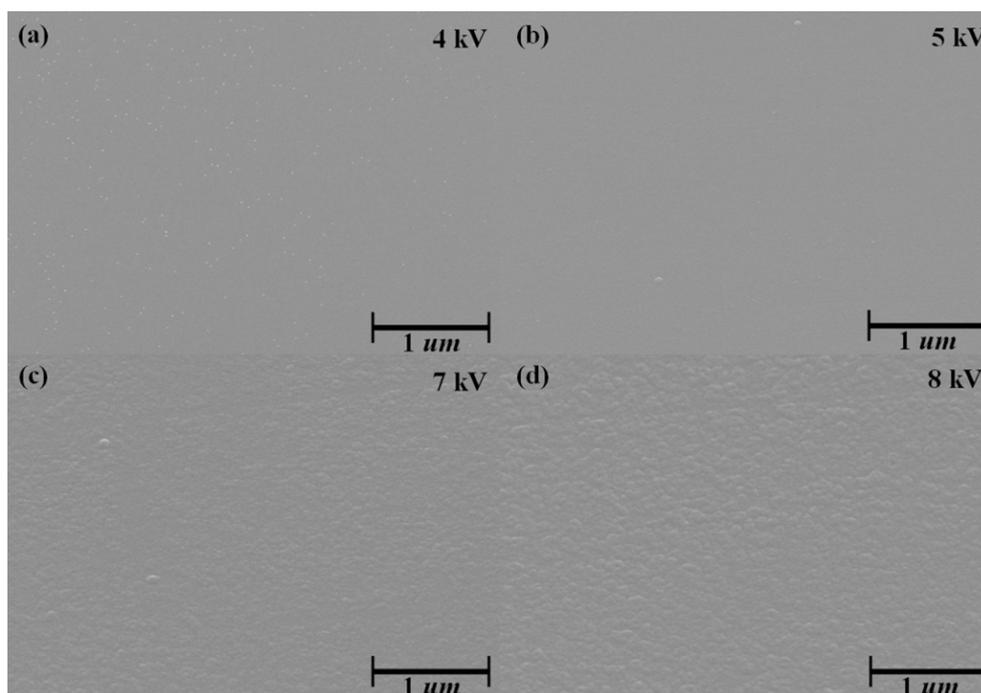


Fig. 5. SEM micrographs of the deposited SiO_x thin films for various applied voltages: (a) 4 kV, (b) 5 kV, (c) 7 kV and (d) 8 kV. The deposition conditions are the same as those shown in Figure 2.

Figures 5(a)~(d) show SEM micrographs of SiO_x thin film surfaces deposited at various applied voltages to the power electrode. A SiO_x thin film was deposited on glass substrates and the thickness was maintained at 200 nm. As shown in Figure 5(a), the surface of the SiO_x deposited at 4 kV was generally smooth, but showed small particles on the SiO_x surface. However, when the applied voltage was higher than 5 kV, as shown in Figures 5(c) and (d), a rough surface could be observed. FTIR data in Figure 3 and XPS data in Figure 4 suggest much Si-OH binding in the SiO_x film deposited at 4 kV and possibly more Si-CH related binding in the SiO_x thin film deposited at applied voltage higher than 5 kV. Also, at the low applied voltage, incomplete and lower dissociation of PDMS was obtained compared to oxygen dissociation and, at high applied voltages, more complete and higher dissociation of PDMS was obtained compared to oxygen dissociation. Therefore, the small particles observed on the SiO_x thin film deposited at 4 kV, as shown in Figure 5(a), is believed to be related to the deposition of incompletely decomposed PDMS itself on the glass surface and the rough surface of SiO_x thin films deposited at applied voltages higher than 5 kV, as shown in Figures 5(c) and (d), appears to be related to the deposition of highly dissociated and agglomerated PDMS without enough oxygen atoms. However, as shown in Figure 5(b), for the SiO_x thin film deposited at 5 kV, a smooth surface could be observed, possibly due to the formation of a stoichiometric SiO_2 -like thin film by the adequate combination of dissociated oxygen and dissociated PDMS.

IV. CONCLUSIONS

SiO_x thin films were deposited using a pin-to-plate DBD type AP-PECVD with PDMS (pre-polymer : curing agent = 10 : 1) polymer source / O_2 gas at substrate temperatures lower than 70 °C as a function of the voltage applied to the power electrode. When the SiO_x was deposited at a low applied voltage of 4 kV, due to the lower dissociation rate of PDMS compared to that of oxygen, a SiO_x thin film containing Si-OH bonding and having a surface with small particles could be observed. However, when the SiO_x was deposited at applied voltages higher than 5 kV, due to the higher dissociation rate of PDMS compared to oxygen, a SiO_x thin film containing Si-CH bonding and having a rough surface could be observed. At an applied voltage of 5 kV, a stoichiometric SiO_2 -like thin film having a low carbon content of 1.5 % and a smooth surface could be obtained at the deposition rate of 12 nm/min for substrate temperatures lower than 50 °C.

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