Study of Atmospheric Pressure Chemical Vapor Deposition by Using a Double Discharge System for SiO_x Thin-film Deposition with a HMDS/Ar/He/O_2 Gas Mixture

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SiO_x thin films were deposited at atmospheric pressure by using a double discharge system composed of a remote-type dielectric barrier discharge (DBD) formed above the substrate and a direct-type DBD formed by applying an AC power to the substrate with a gas mixture of hexamethyldisilazane (HMDS)/O_2/He/Ar. Instead of using a single DBD, the use of the double discharge system not only showed higher SiO_x thin film deposition rates but also produced fewer impurities in the deposited SiO_x thin film. The improvement was partially related to the increased gas dissociation near the substrate through the direct-type DBD and to the remote-type DBD. A 7-kV, 30-kHz AC voltage was applied to the remote-type DBD and a 5-kV, 20-kHz AC voltage was applied to the direct-type DBD, with a gas mixture of HMDS (400 sccm)/O_2 (20 slm)/He (5 slm)/Ar (3 slm). As a result, a SiO_x deposition rate of 58.29 nm/scan could be obtained while moving the substrate at a speed of 0.25 meter/min.

I. INTRODUCTION

Silicon-oxide thin films are used extensively for their outstanding material characteristics, such as high chemical stability, high hardness, high scratch resistance, and specific dielectric properties [1–3]. For electronic applications, the material has many potential applications, including gate dielectric materials, inter-metal dielectric materials, and passivation and gas barrier-layer thin films to protect from mechanical and chemical attack [3,4]

In most cases, SiO_x thin films are deposited by using chemical vapor deposition (CVD) because high-quality material characteristics and good step coverage can be obtained. Plasma enhanced CVD (PECVD) is applied to deposit SiO_x thin film at a low temperature [5]. However, in general, the deposition of a thin film by using PECVD requires a vacuum system, which is not only expensive but also causes the process to be slow due to the need for a loadlock system [3,6-8]. Moreover, an extremely large-scale PECVD system applied to flat panel displays is extremely expensive, and to obtaining uniformly deposited materials on the substrate is difficult with this method. Therefore, for the next generation of electronic materials processing, it would be beneficial if SiO_x thin films could be deposited by in-line processing using atmospheric pressure PECVD (AP-PECVD).

Many different kinds of plasma sources have been investigated for various processes at atmospheric pressure, including radio-frequency plasma torches, dielectric barrier discharges (DBDs), microwave discharges, and pulsed corona plasmas [9]. Among these, DBD sources, which consist of two parallel electrodes, have been investigated because they are uniform and have large-area glow discharges [10]. Especially, DBDs have been studied for flexible display device processing using roll-to-roll systems operated without expensive vacuum pumps, vacuum gauges, or loadlock systems [11,12].

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Direct-type DBDs are commonly used and have one electrode that is grounded and AC power that is applied to the other electrode to generate a capacitively-coupled plasma. The direct-type DBD process is known to tend to show good process efficiencies because the substrate is directly exposed to the atmospheric discharge [13]. However, during the processing, the substrate can be easily damaged by filamentary discharges, especially these formed during high-process-rate conditions [14,15]. The possible damage can be easily reduced by using a remote-type DBD where the substrate is not directly exposed to the atmospheric pressure plasma [16]. However, the use of the remote-type DBD tends to decrease the deposition rate and tends to cause porosity in the deposited material, especially when the material is deposited at a low temperature such as room temperature [15].

Previously, a double-discharge system composed of a direct-type DBD and a remote-type DBD had been investigated to improve the characteristics of the deposited SiO_x material without decreasing the deposition rate when using an $HMDS/He/O_2/Ar$ gas mixture [1,17]. To form the double-discharge system, in addition to the remote-type DBD, a direct-type DBD was formed by applying additional power, such as AC power or pulse power, to the substrate. By increasing the power to the substrate and by increasing the pulse power frequency, improved characteristics of the deposited SiO_x thin film could be obtained. By using the double-discharge, the possibility of substrate damage caused by the filamentary discharge, which is observed during the operation of a direct-type DBD system, is significantly decreased because the main discharge is still the remote-type DBD and because the direct-type DBD in the double discharge is an auxiliary discharge, which induces not only more ionization and dissociation of the gas mixture but also ion bombardment on the substrate. Therefore, by using the double discharge system, a significant decrease in the substrate damage can be expected. In this study, the effect of AC voltage on the characteristics of the deposited SiO_x thin film and on the plasma characteristics were investigated with an $HMDS/He/O_2/Ar$ gas mixture to find the process window for improving the characteristics of the SiO_x thin film deposited by using the double-discharge system.

II. EXPERIMENTAL DETAILS

SiO_x thin films were deposited by using AP-PECVD with a double-discharge system that consisted of a direct-type DBD source and a remote-type DBD source. A schematic diagram of the system is shown in Fig. 1. The remote-type DBD source was composed of three flat metal electrodes covered with 3-mm-thick ceramic plates for the dielectric layer (two remote-type DBDs). On the outside were two flat metal electrodes covered with a dielectric layer to which an AC voltage in the
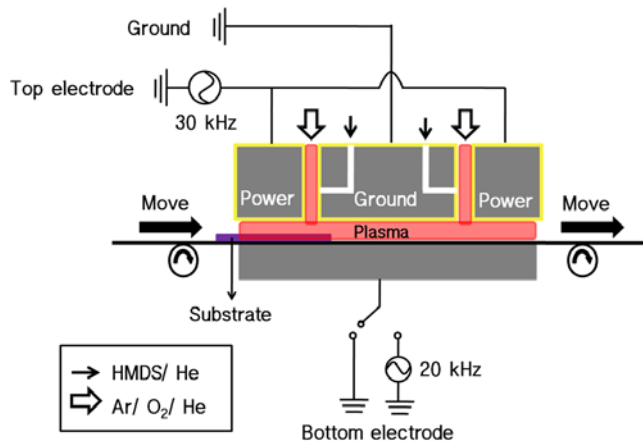

Fig. 1. (Color online) Schematic diagram of the double discharge system used to deposit the SiO_x thin film. The system consisted of a remote-type DBD source above the substrate (two remote-type DBDs) and a direct-type DBD on the substrate, with additional AC power applied to the substrate electrode.

range $4 \sim 7$ kV (30 kHz) was applied; the middle flat metal electrode was grounded to form a dual remote-type DBD. The air gap between the electrodes was about 1.5 mm. Under the remote-type DBD, the substrate electrode, which was covered with 1-mm-thick quartz, was located on the substrate and was grounded or connected to a separate AC power source (20 kHz, 5 kV) to form a direct-type DBD, in addition to the remote-type DBD.

Hexamethyldisilazane (Sigma-Aldrich Co., purity 99.9%, $Si_2NH(CH_3)_6$) was used as the Si source and was delivered to the double-discharge system through the holes located on the bottom side of the middle ground electrode of the remote-type DBD source to decrease the possible deposition at the sidewall of the remote-type DBD source. Helium was used as a carrier gas for the delivery of HMDS through the bubbler. A gas mixture of $Ar/O_2/He$ was separately fed through the top side of the remote-type DBD. Consequently, a gas mixture composed of HMDS (400 sccm)/O_2 (20 slm)/He (5 slm)/Ar (3 slm) was used to deposit the SiO_x thin films on the Si wafer located on the substrate electrode. The substrate temperatures during the AP-PECVD remained at about 80 °C. The substrates were continuously moving at a speed of 0.25 m/min for the in-line deposition.

After the deposition, the chemical binding structure of the SiO_x thin films was observed by using a Fourier transform infrared spectrometer (FT-IR, Bruker, IFS-66/S). The binding states and the compositions of the deposited SiO_x thin films were observed by using X-ray photoelectron spectroscopy (XPS, Thermo Electronics, Multilab ESCA2000). Also, the plasma characteristics were observed by using optical emission spectroscopy (OES, SC-Technology, PCM 420).
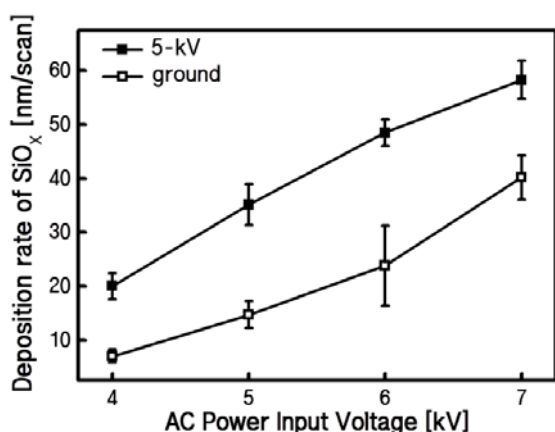
Fig. 2. Deposition rate of SiO_x thin films as a function of AC power input voltages from $4 \sim 7$ kV (30 kHz) to the remote-type DBD source while the substrate is grounded or powered by a 5-kV (20 kHz) AC voltage to form a double discharge.
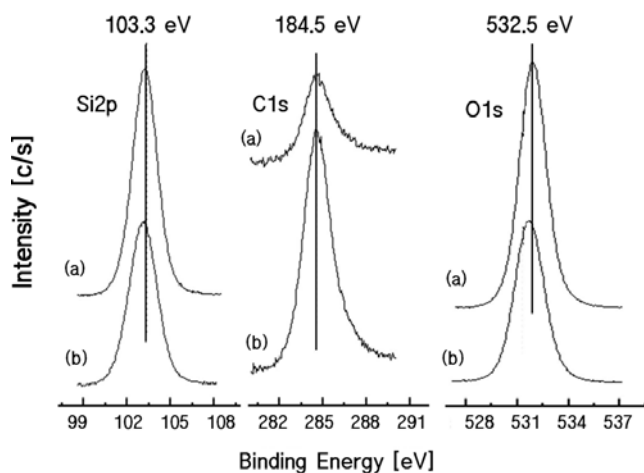

Fig. 3. XPS narrow scan data on silicon, carbon, and oxygen for SiO_x thin films deposited by applying a 7-kV, 30-kHz AC voltage to the remote-type DBD while the substrate electrode is (a) powered by a 5-kV, 20-kHz AC voltage to form a direct-type DBD or is (b) grounded.

III. RESULTS AND DISCUSSION

Figure 2 shows the SiO_x deposition rates measured as functions of the 30-kHz AC power input voltage of the remote-type DBD source. As shown in Fig. 2, when the ground electrode was connected, the SiO_x deposition rate increased from 7 to 36.1 nm/scan as the AC voltage on the remote-type DBD source was increased from 4 to 7 kV. The increase in the AC voltage produced a significant increase in the deposition rate of the SiO_x, but when a separate 20-kHz AC voltage of 5 kV was applied to the substrate electrode to form a direct-type DBD, in addition to the remote-type DBD, the deposition rate of the SiO_x thin film was further increased from 20 to 58.3 nm/scan for an increase in the AC voltage to the remote-type DBD source from 4 to 7 kV. The increase in the SiO_x deposition rate with increasing AC power to the remote-type DBD source is related to the increased a gas dissociation of O_2 and HMDS while passing through the gap of the remote-type DBD source. The application of the AC voltage to the substrate electrode, in addition to the remote-type DBD, not only increased the gas dissociation by forming a separate plasma near the substrate but also increased the discharge area from the two gap lines of the remote-type DBDs to the surface covering all of the substrate electrode.

Figure 3 shows the XPS narrow scan data for silicon, carbon, and oxygen in the SiO_x thin films for conditions when the substrate electrode was (a) powered by a 5-kV, 20-kHz AC voltage to form a direct-type DBD or was (b) grounded. The Si_{2p} binding peak, the C_{1s} peak, and the O_{1s} peak located at 103.3 eV, 284.5 eV, and 532.5 eV, respectively, were investigated to measure the chemical binding states and the compositions of the deposited SiO_x thin films [16,18,19]. As shown in Fig. 3, the peak intensity of Si_{2p} was increased by the for-

mation of the double discharge, indicating an increased silicon percentage in the deposited film. Also, the Si_{2p} binding energy peak in the SiO_x deposited with the double discharge was higher than that in the SiO_x deposited with the remote-type DBD only and was close to the thermally-grown SiO_x binding energy peak of 103.3 eV [16]. The second image in Fig. 3 shows the C_{1s} binding peaks in the films deposited with the double discharge and with the remote-type discharge only. After the application of 5-kV, 20-kHz AC power to the substrate, a decrease in the C_{1s} peak could be observed, indicating a reduction of carbon impurity in the deposited SiO_x caused by the increased dissociation of HMDS and O_2 in the plasma. Also, as shown in the right figures, the use of the double discharge increased the oxygen percentage in the deposited SiO_x. The double discharge also increased the O_{1s} binding peak position to close to 532.5 eV, which indicates an increase in Si-O bonding in the deposited SiO_x thin film, which is similar to the change in the Si_{2p} binding energy position produced by the application of 5-kV, 20-kHz AC power to the substrate [19].

Figure 4 shows the chemical binding structure of SiO_x measured by using FT-IR for the SiO_x thin films deposited with the conditions in Fig. 3. The top and the bottom figures show the FT-IR data for the SiO_x thin films deposited with the double-discharge DBD and the remote-type DBD only, respectively. The peak in the range of $1020 \sim 1070$ cm^{-1} [20] is the peak related to Si-O-Si binding; the peaks in the ranges of $900 \sim 960$ cm^{-1} and $3250 \sim 3746$ cm^{-1} [21,22] are related to Si-OH binding; and the peaks in the ranges of $840 \sim 852$ cm^{-1} and 1246 cm^{-1} ~ 1256 cm^{-1} [20,23,24] are related to Si-$(CH_3)_3$ and Si-$(CH_3)_x$ bindings, respectively. As shown, the peak related to Si-OH binding was not changed significantly after the application of 5-kV, 20-
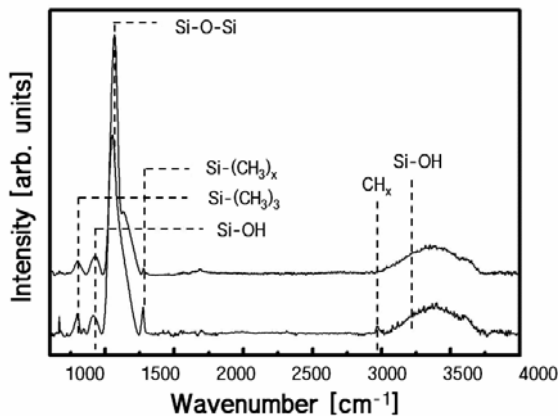
Fig. 4. FT-IR spectra of the SiO_x thin films deposited with the conditions shown in Fig. 3.
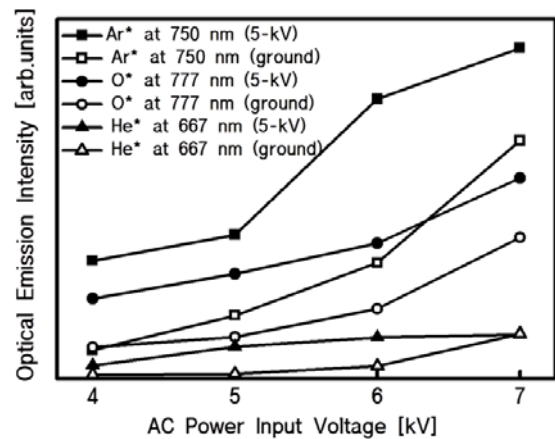

Fig. 5. Relative OES peak intensities of Ar, O, and He measured near the substrate as a function of the remote-type DBD source power while the substrate is grounded or a 5-kV, 20-kHz AC power is applied to the substrate.

kHz AC power to the substrate. However, as shown, an increase in the Si-O-Si binding peak was observed by the use of a double-discharge DBD instead of the remote-type DBD only, while the binding peaks related to Si-$(CH_3)_3$, Si-$(CH_3)_x$, and CH_x decreased due to increased oxidation of HMDS caused by the increased dissociation of HMDS and O_2, similar to the results shown in Fig. 3. Binding peaks such as Si-$(CH_3)_3$, Si-$(CH_3)_x$, and CH_x tend to decrease the density of the deposited film. Therefore, by the use of the double-discharge DBD instead of only the remote-type DBD, not only is there a decrease of impurities such as C and H in the deposited SiO_x thin film but also an increase in the SiO_x thin film density can be obtained. The improved properties of the deposited SiO_x thin film are believed to be partially related to the increased dissociation of HMDS and oxygen near the substrate surface due to the application of the AC power to the substrate in addition to the use of the remote-type DBD. The ion-bombarding effect caused by the application of the AC power to the substrate, which was observed in previous research [1], can also affect the improvement of the SiO_x thin-film properties.

To investigate the differences in the discharge characteristics between the double-discharge DBD and the remote-type DBD only, we measured the optical emission spectroscopic data for Ar, O, and He, which are included in the deposition gas mixture. Figure 5 shows the OES peak intensities of the Ar, O, and He measured near the substrate as functions of the 30-kHz AC power to the remote-type DBD source while applying 5-kV, 20-kHz AC power to the substrate and while grounding the substrate. The optical emission intensities related to HMDS could not be measured due to the complexity of the molecular structure even after the dissociation. Instead, the optical emission peaks related to Ar, O, and He were measured and observed at wavelengths of 750, 777, and 667 nm, respectively [25–27]. As shown in the figure, an increase in the AC power to the remote-type DBD source increased the optical emission intensities of

Ar, O, and He, possibly indicating increased dissociation of HMDS in addition to increased dissociation of oxygen. Especially, as shown in the figure, the addition of a 5 kV, 20-kHz AC voltage to the substrate further increased the optical emission intensities of Ar, O, and He, indicating further gas dissociation by the use of the double discharge DBD caused by the increased plasma density near the substrate.

IV. CONCLUSION

In this study, SiO_x thin films were deposited at a temperature lower than 80 °C by using a double discharge composed of a remote-type DBD and a direct-type DBD with a gas mixture composed of HMDS (400 sccm)/O_2 (20 slm)/He (5 slm)/Ar (3 slm), and the effect of the AC voltage to the remote-type DBD (in addition to the direct-type DBD) on the deposited SiO_x thin-film characteristics and the plasma characteristics was investigated. The SiO_x deposition rate increased with increasing AC power to the remote-type DBD and with addition of the direct-type DBD on the substrate. Therefore, by forming a double discharge, a further increase in the SiO_x deposition rate could be obtained. By using the double discharge, in addition to the increase in the SiO_x deposition rate, an improvement in the SiO_x thin-film characteristics, such as a decrease in impurity, an increase in Si-O binding, and an improvement in the film's density, by decreasing the Si-$(CH_3)_3$, Si-$(CH_3)_x$, and -$(CH)_x$ binding could be obtained. The improvement in the film characteristics caused by adding the direct-type DBD is believed to be related to the increased dissociation of HMDS and oxygen near the substrate caused by the additional discharge forming near the substrate because of using the direct-type DBD and to the possible ion bombardment of the substrate caused by the AC

power applied to the substrate. The increased optical emission intensities with increasing AC power, both to the remote-type DBD source and to the substrate, are believed to be related to the increased gas dissociation through the increased plasma density caused by increasing the AC power to both electrodes.

ACKNOWLEDGMENTS

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