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Ion Bombardment during the Deposition of SiO_X by AC-Biasing in a Remote-Type Atmospheric Pressure Plasma System

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The effect of the additional ac-bias voltage applied to the substrate on the characteristics of the SiO_X deposited using modified remote-type atmospheric pressure plasma at room temperature was investigated for the gas mixture of hexamethyldisilazane/O_2/He/Ar. The addition and increase of ac-bias voltage not only increased the deposition rate but also improved the characteristics of the deposited SiO_X. With the increase of ac-bias voltage to the substrate, the oxygen percentage in the film increased while the carbon percentage is decreased by increasing Si–O–Si bonding and by decreasing the impurity such as $-(CH_3)_X$ in the deposited film. In addition, the hardness and the surface smoothness of the deposited film were also increased with the increase of the ac biasing. The improvement of the film properties was related to the ion bombardment effect in addition to the increased gas dissociation by the additional power absorption, which was caused by the ac biasing of the substrate.
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Silicon oxide films are of great interest because of their excellent physical and chemical properties such as high scratch resistance and hardness, high chemical inertness, high optical transparency,[1] etc. They are widely used in many fields of industrial applications such as dielectric materials for electronic devices, corrosion protection layers for mechanical structures, passivation layers for electronic device substrates, and food packing.[2-4]

For the formation of silicon oxide thin films on a substrate, various physical and chemical vapor deposition methods, such as thermal oxidation of silicon, plasma enhanced chemical vapor deposition (PECVD),[5] sputter deposition, evaporation, ion beam assisted evaporation, etc. have been studied. Among these methods, low pressure plasma enhanced chemical vapor deposition (LP-PECVD) is one of the methods that can be used to deposit the materials at low temperatures on a large area uniformly with good step coverage and a high deposition rate.[6-8] Silicon oxide films deposited by LP-PECVD have been extensively studied over the years, leading to a significant optimization of film stoichiometry, density, and hardness.[9] A limitation of this technology, however, is generally the need for expensive and complicated vacuum systems, which limits the materials' processing capability to expensive, vacuum-compatible materials.[4]

In this respect, the atmospheric pressure plasma enhanced chemical vapor deposition (AP-PECVD) is considered as an emerging technology which not only offers advantage in cost reduction due to the lack of bulky and expensive vacuum equipment, but also is compatible for continuous production lines and large-scale operation.[10] Among the various AP-PECVD techniques,[11] dielectric barrier discharge (DBD) is widely investigated due to its easier generation of a uniform glow discharge on a large substrate area. In addition, DBD is known to be one of the most suitable plasma generation modes for inline systems because it is cold, robust, and not significantly disturbed by the movement of the substrate.[12,13] However, when DBD is applied to the PECVD of SiO_X, especially on low temperature substrates such as plastic substrates using the gas mixtures such as tetraethoxysilane (TEOS)/O_2/He (Ar, etc.), hexamethyldisilazane (HMDS)/O_2/He (Ar, etc.), polydimethylsiloxane (PDMS)/O_2/He (Ar, etc.) etc. which has $-(CH_3)_X$ in the gas mixture, the deposited SiO_X contains significant amount of carbon due to the difficulty in the sufficient dissociation of the silicon-containing gases and oxygen molecule. The increase of oxygen in the gas mixture to decrease carbon in the depositing SiO_X finally causes a filamentary discharge, which leads to the damage to the substrate in addition to the decrease of deposition rate.[14,15] Even when the remote-type AP-PECVD is used to avoid the possible damage by the filamentary discharge to the plastic substrate during the deposition of SiO_X, the decrease in the deposition rate in addition to the porous material property is also obtained.[16]

In our recent research, by the application of an additional DBD on the substrate during the deposition of SiO_X by a remote-type AP-PECVD inline system having a modified DBD source (that is, by using a double-discharge system), the increase of SiO_X deposition rate in addition to the improvement of SiO_X properties such as the decrease of carbon content, the increase of oxygen content, etc. could be obtained.[17] The improvement of the physical and chemical properties of the deposited SiO_X can originate from the additional discharge on the substrate which increases the dissociation of the gas mixture but it also could be from the effect of ion bombardment caused by the ac voltage applied to the substrate. In this study, the effect of various ac-bias voltages applied to the substrate during the deposition of SiO_X by a remote-type AP-PECVD on the physical and chemical properties was investigated systematically to clarify the origin of the improvement of the material properties by the application of ac voltage to the substrate.

Experimental

A schematic diagram of the experimental setup used to deposit the SiO_X films is shown in Fig. 1. The remote-type DBD source for AP-PECVD consisted of three flat metal electrodes. All of the electrodes were covered with 3 mm ceramic plates for dielectric layer and the ground electrode [(b); 60 × 130 × 40 mm] was located at the center area while the two power electrodes [(a) and (c); 25 × 130 × 40 mm] were located at the outside for the formation of a remote-type DBD source. For the ac-biasing, another electrode [(d); 113 × 130 × 20 mm] covered with a 1.5 mm quartz plate was located at the bottom of the remote-type source and below the substrate as shown in the figure. The remote-type atmospheric pressure plasmas were generated by applying 30 kHz 7 kV ac power to the power electrodes [(a) and (c)] of the remote-type AP-PECVD source. The substrate electrode (d) was grounded or ac-biased using a 20 kHz ac power supply from 4 to 8 kV.

As the silicon precursor, HMDS [Sigma-Aldrich Co, purity 99.9%, $Si_2NH(CH_3)_6$] was used and was delivered to the source using He as a carrier gas. A gas mixture composed of HMDS (400 sccm delivered by He)/O_2 (20 slm)/He (5 slm)/Ar (3–13 slm) was used to deposit the SiO_X thin films, where the mixture of He/Ar was used as the discharge gas and O_2 was used for the oxidation of

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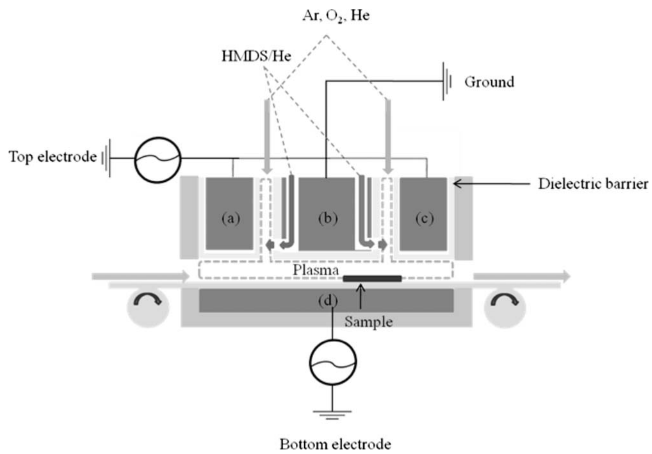

Figure 1. Schematic diagram of the AP-PECVD inline system with a remote-type modified DBD source and ac-biased substrate used to deposit the SiO_X films.

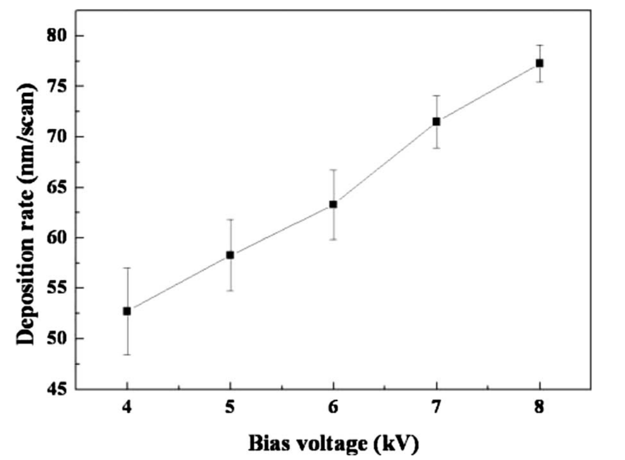

Figure 2. Effect of ac-bias voltage (4–8 kV, 20 kHz ac power) to the substrate on the deposition rate of SiO_X thin film. HMDS (400 sccm)/O_2 (20 slm)/He (5 slm)/Ar (3 slm) was flowed to the remote-type modified DBD source operated at 7 kV, 30 kHz.

HMDS. SiO_X was deposited on the silicon wafer at room temperature without heating. The temperature of the silicon substrate remained at about 50°C even after the exposure to the plasma. The silicon substrates were moving at the speed of 0.3 m/min during the processing.

The thickness of the deposited film was measured using a step profilometer (Tencor, Alpha step 500). The atomic percentage and chemical bonding states of the films were measured by X-ray photoelectron spectroscopy (XPS, Thermo Electronics, Multilab ESCA2000) and Fourier transform infrared spectrometry (Bruker, IFS-66/S) respectively. A Mg source was used as the X-ray source for XPS. Optical emission intensities of the species emitted from the plasma were measured using an optical emission spectroscope (SC-Technology, PCM 420). The hardness of the films was measured at a normal load of 30 mN using a commercially available nanoindentation instrument (MTS, Nano-indenter II). The surface roughness of the deposited SiO_X thin film was observed by atomic force microscopy (AFM; XE 100). The deposited SiO_X thin films were etched in atmospheric pressure etching equipment using N_2 (40 slm)/He (1 slm)/NF_3 (500 sccm) and at 2 kW of 40 kHz pulse power.

Results and Discussion

Figure 2 shows the effect of ac-bias voltage to the substrate on the deposition rate of SiO_X. As the gas mixture, HMDS (400 sccm)/O_2 (20 slm)/He (5 slm)/Ar (3 slm) was used to deposit SiO_X. On the remote-type DBD source, 30 kHz 7 kV ac power was applied while the substrate electrode was ac-biased from 4 to 8 kV with 20 kHz ac power. As shown in Fig. 2, the increase of ac-bias voltage increased the deposition rate from 53 to 77 nm/scan when the ac-bias voltage was increased from 4 to 8 kV. By increasing the 20 kHz ac-bias voltage to the substrate while operating the remote-type DBD, the SiO_X deposition rate was significantly increased.

For the SiO_X thin films deposited as a function of ac-bias voltage in Fig. 2, the change of the atomic composition such as oxygen, silicon, and carbon in the film was investigated by XPS and the results are shown in Fig. 3. As shown in the figure, the silicon percentage was about 27% and, with increasing the ac-bias voltage, no significant change of silicon atomic percentage was observed. However, oxygen percentage was increased from 64 to 71% and the carbon percentage was decreased from 8 to about 1% with increasing the ac-bias voltage to the substrate from 4 to 8 kV. By increasing the ac-bias voltage, the deposited SiO_X not only increased the SiO_X deposition rate but also showed the SiO_X films with less carbon impurity content by replacing carbon with oxygen.

The chemical bonding states of the SiO_X thin films deposited as a function of ac-bias voltage were investigated using FTIR and the results are shown in Fig. 4a for the Si–O–Si bonding at around 1075 cm^{-1},[18] Fig. 4b for the Si–$(CH_3)_X$ bond at 1246–1260 cm^{-1},[19] and Fig. 4c for the Si–OH bonding at 3250–3600 cm^{-1}.[16] The thickness of the deposited SiO_X thin film was maintained at 200 nm. As shown in Fig. 4a-4c, with the increase of ac-bias voltage, the peak intensity originated from Si–$(CH_3)_X$ was decreased while the bonding peak related to Si–O–Si bonding was increased due to the decrease of carbon and the increase of oxygen with the increase of ac-bias voltage. The Si–OH bonding peak intensity was not significantly varied with the increased of ac-bias voltage.

The increase of deposition rate, the decrease of carbon percentage and the increase of oxygen percentage in the deposited SiO_X film, and the increase of Si–O–Si bonding in the deposited SiO_X thin film with the decrease of Si–$(CH_3)_X$ bonding observed in Fig. 2-4 with the increase of the ac-bias voltage to the substrate are partially related to the increase of the plasma density and the gas dissociation caused by the additional power input to the gas mixture near the substrate area by applying higher ac power to the substrate. Figure 5 shows the optical emission spectra (OES) peak intensities of He (587.6 nm),[20] Ar (750 nm),[21] and O (777 nm) (Ref. 22) near the substrate measured as a function of ac-bias voltage for the gas mixture of HMDS (400 sccm)/O_2 (20 slm)/He (5 slm)/Ar (3 slm) used

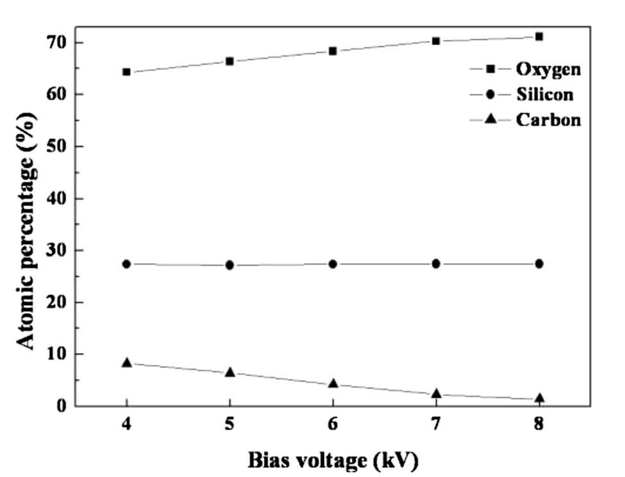

Figure 3. Atomic percentage of the deposited SiO_X thin film investigated by XPS as a function of ac-bias voltage from 4 to 8 kV. The other deposition conditions are the same as those in Fig. 2.

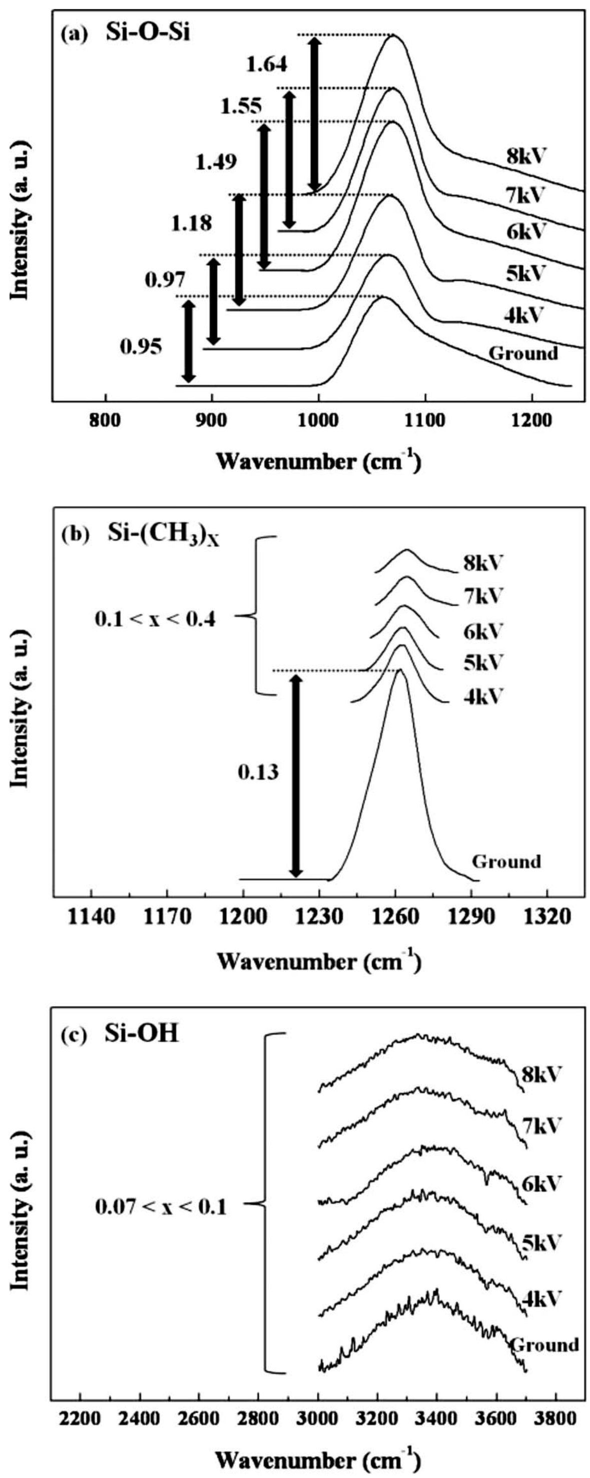

Figure 4. FTIR spectra of the SiO_X thin films deposited at various ac-bias voltages. Thickness of the deposited SiO_X thin film was kept at 200 nm. The other deposition conditions are the same as those shown in Fig. 2. (a) for Si–O–Si bonding, (b) for Si–$(CH_3)_X$ bonding, and (c) for Si–OH bonding.

in the experiment. The experimental conditions are the same as those in Fig. 2. Due to the difficulty in the measurement of the signals for the experimental configuration, only the atomic emission peak intensities of He, Ar, and O could be measured. As shown, the increase of ac-bias voltage to the substrate increased the atomic peak intensities of He, Ar, and O near the substrate almost linearly, possibly due to the increase of plasma density and oxygen molecule

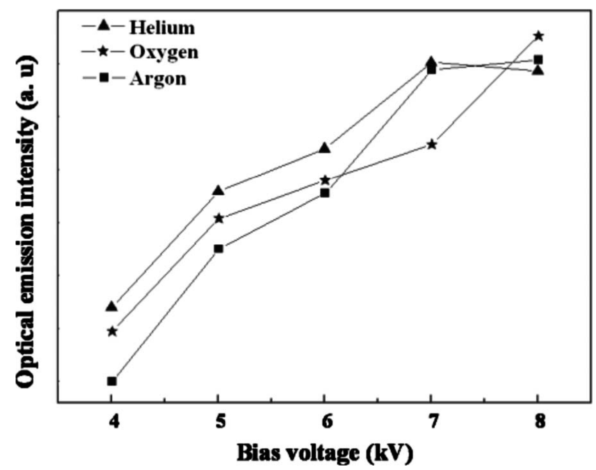

Figure 5. Relative optical emission intensities measured as a function of ac-bias voltage. The operating conditions are the same as those shown in Fig. 2.

dissociation through the increased power absorption with the increase of ac-bias voltage, even though the increased oxygen atomic OES peak intensity does not provide direct evidence of the increased dissociation of oxygen molecule. The increased dissociation of gas molecules such as oxygen molecule and HMDS molecule by the increased power absorption with the increase of ac-bias voltage can increase the SiO_X deposition rate by the increased formation of SiO_X on the substrate through the increased influx of dissociated species on the substrate surface. It can also decrease the carbon percentage and increase the oxygen percentage in the deposited SiO_X by removing $-(CH_3)_X$ bondings on the SiO_X film surface by the increased reaction of carbon in HMDS with oxygen from oxygen molecule.

The addition and increase of ac-bias voltage to the substrate not only improved the deposition rate and the stoichiometry of the deposited SiO_X thin film but also improved the density of the deposited SiO_X thin film. The change of SiO_X density with the increase of ac-bias voltage was indirectly investigated using an etching experiment and by measuring hardness of the deposited SiO_X thin films. The thickness of the deposited SiO_X thin film was maintained at 250 nm before the measurements. The deposited SiO_X thin films were etched in atmospheric pressure etching equipment and the results are shown in Fig. 6. As shown in the figure, the increase of

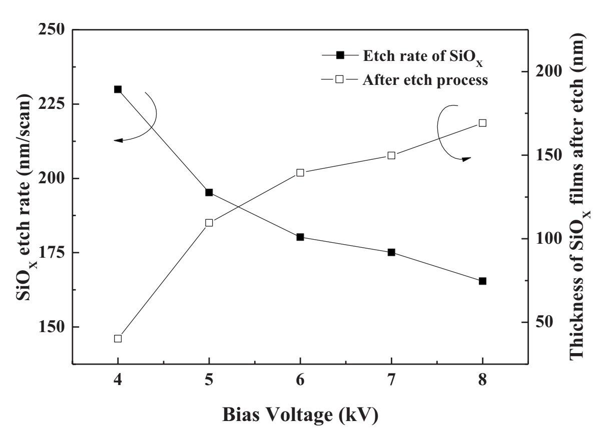

Figure 6. Etch rate of the SiO_X deposited as a function of ac-bias voltage in atmospheric pressure etching equipment in N_2 (40 slm)/He (1 slm)/NF_3 (500 sccm) and using 2 kW of 40 kHz pulse power. The SiO_X deposition conditions are the same as those shown in Fig. 2.

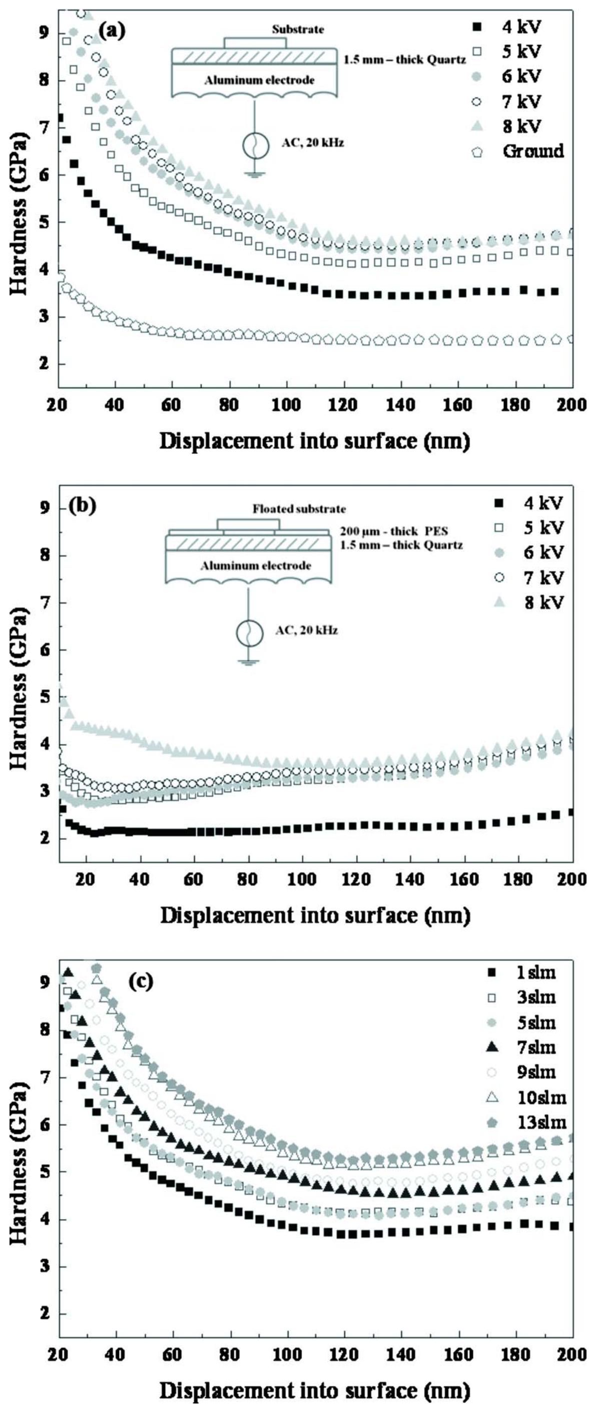

Figure 7. (Color online) Hardness measured as a function of ac-bias voltage. The thickness of the deposited SiO_X was maintained at 300 nm. The other conditions were the same as those shown in Fig. 2. SiO_X thin film was deposited (a) on the substrate attached to the ac-biased electrode or (b) on the substrate floated about 200 μm above the ac-biased electrode. (c) The effect of Ar flow rate in HMDS (400 sccm)/O_2 (20 slm)/He (5 slm)/Ar (x slm) on the hardness of the deposited SiO_X thin film. The ac-bias voltage was kept at 5 kV while other deposition conditions were maintained the same as those in Fig. 6a.

ac-bias voltage from 4 to 8 kV decreased the SiO_X etch rate from 230 to 165 nm/scan, indirectly indicating higher SiO_X film density at the higher ac-bias voltage.

Figure 7a shows the hardness of the SiO_X thin film deposited as a function of ac-bias voltage from 4 to 8 kV as the other indirect indication of SiO_X density. The hardness of SiO_X deposited while grounding the substrate was also included. The SiO_X deposition conditions are the same as those in Fig. 2. The thickness of the deposited SiO_X thin film was maintained at 300 nm and the indenter tip was displaced 2 nm each time into the SiO_X thin film for 100 times (to 200 nm in depth) to measure the hardness of thin film through the relationship between the load and the displacement into the film. The stabilized hardness value was the lowest at about 2.6 GPa for the SiO_X deposited while grounding the substrate and the increase of ac-bias voltage generally increased the hardness of the deposited SiO_X thin film up to 4.6 GPa for the thin film deposited with 8 kV of ac-biasing. The improvement of SiO_X hardness and the decreased SiO_X etch rate are related to the increase of SiO_X density, and the increase of SiO_X thin film density with the addition and increase of ac-bias voltage can be also partially related to the removal of the bondings in SiO_X thin film such as $-(CH_3)_X$ by the increased dissociation of gas molecules with the addition and increase of ac-bias voltage to the substrate because these bondings tend to show porosity in the film.[23]

The improvement of hardness with the addition and increase of ac-bias voltage to the substrate can be partially related to the increased gas dissociation due to the additional power absorption above the substrate as mentioned above. However, it could be also related to the increased ion bombardment to the substrate by the ac-bias voltage because the sheath holding the electric field with the distance larger than a few tens of micrometers exists during the operation of ac-biasing[24,25] even though the mean free path is only several tens of nanometers. To investigate the possibility of ion bombardment during the SiO_X deposition by ac-biasing, the SiO_X was also deposited at the same condition as those in Fig. 7a but by floating the substrate above the ac-biased electrode about 200 μm with a poly ether sulphone (PES), as shown in the inset of Fig. 7b. Figure 7b shows the hardness measured for the SiO_X deposited with the floated substrate and, as shown in Fig. 7b, the hardness of the SiO_X deposited at the same condition as that in Fig. 7a decreased more than 20%, which is related to the decrease of ion bombardment during the deposition of SiO_X thin film. Therefore, it is believed that the ion bombardment by ac-biasing not only increased the hardness but also improved the other properties such as deposition rate shown in Fig. 2-4 by the increased reactivity on the surface during the deposition of SiO_X thin film.

The inert gases in the gas mixture such as He and Ar used in the experiment are important not only in generating glow discharges but also in maintaining the plasma stability.[26] Especially, Ar can be also effective in the ion bombardment of the substrate due to its heavy mass. Figure 7c shows the effect of Ar flow rate in HMDS (400 sccm)/O_2 (20 slm)/He (5 slm)/Ar (x slm) on the hardness of the deposited SiO_X thin film. The ac-bias voltage was kept at 5 kV while other deposition conditions were maintained the same as those in Fig. 7a. As shown in the figure, the increase of Ar gas flow rate from 1 to 13 slm in the gas mixture increased the hardness of deposited SiO_X from 3.6 to 5.4 GPa, which appears to be related to the increased ion bombardment by the increased Ar ion density with the increase of Ar flow rate in the plasma.

For the SiO_X thin films deposited as a function of ac-bias voltage from 4 to 8 kV with the deposition conditions in Fig. 7a, the surface roughness was measured by AFM using a noncontact mode, and the results are shown in Fig. 8. The surface roughness was the highest at 3.78 nm for the SiO_X deposited at the lowest voltage of 4 kV and it decreased with increasing ac-bias voltage to 1.81 nm at 8 kV. The decrease of surface roughness with the increase of ac-bias voltage to the substrate can be partially related to the removal of impurity bondings such as $-(CH_3)_X$ in the film by the increased gas dissociation with the increased ac-biasing. However, it is more related to the increased ion bombardment which increases the surface reactions by adding extra energy on the surface, increases the surface migration of the adsorbed species, and helps in desorbing the reac-

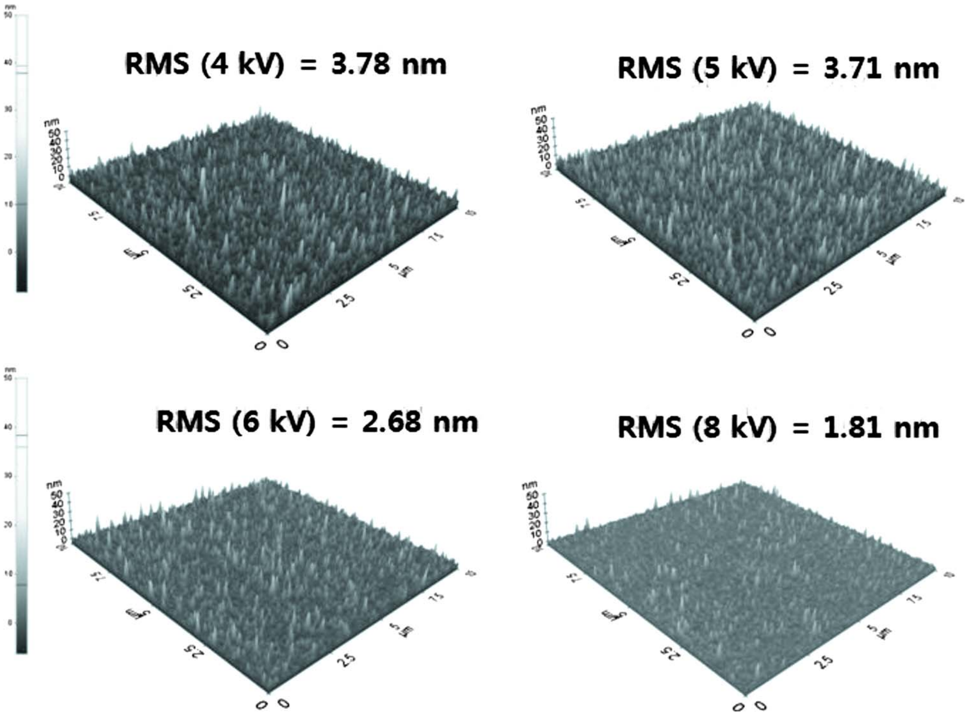

Figure 8. (Color online) Surface roughness of SiO_X film deposited by AFM as a function of ac-bias voltage. The deposition conditions are the same as those shown in Fig. 2.

tion products in addition to the surface smoothing that is occurred similarly by sputter etching in a low pressure plasma.[27]

Conclusions

In this study, the effect of ac-biasing to the substrate during the deposition of SiO_X thin films in an AP-PECVD system with a remote-type DBD on the characteristics of the SiO_X thin film were investigated using a gas mixture of HMDS (400 sccm)/O_2 (20 slm)/He (5 slm)/Ar (1–13 slm).

The increase of ac-bias voltage to the substrate not only increased the deposition rate but also decreased the carbon percentage and increased the oxygen percentage in the deposited SiO_X thin film by removing the impurity bonds such as $-(CH_3)_X$ in the film. The increase of ac-bias voltage also increased the density of the deposited SiO_X thin film and the decreased surface roughness. The improvement of the physical and chemical properties of the deposited SiO_X thin film with the increase of ac-bias voltage to the substrate was partially related to the increased gas dissociation and reaction due to the increased plasma density through the power absorption above the substrate by the additional DBD on the substrate. However, the improved physical and chemical properties of the SiO_X deposited with the ac-biasing was more related to the ion bombardment effect by showing worse physical and chemical properties when the SiO_X was deposited on the floated substrate having lower ion bombardment energy while other deposition conditions were maintained the same. The increased hardness with increasing Ar flow rate in the gas mixture and the improved surface smoothness with the increase of ac-bias voltage are also believed to be caused more by the increased ion bombardment effect.

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