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Characteristics of SiO_X thin films deposited by atmospheric pressure chemical vapor deposition using a double-discharge system

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ABSTRACT

SiO_X thin films were deposited using a gas mixture of hexamethyldisilazane (HMDS)/O_2/He/Ar from a remote-type dielectric barrier discharges (DBD) source, with/without the additional direct-type DBD just above the substrate (double discharge), and the effect of the double discharge on the characteristics of the SiO_X thin film was investigated. The increase of HMDS flow rate and the decrease of oxygen flow rate in the gas mixture increased the SiO_X-thin-film deposition rate. The improvement of the mechanical properties for SiO_X film, in addition to the increase of deposition rate, is believed to be related not only to the higher gas dissociation because of the higher power deposition but also to the lesser recombination of oxygen atoms and dissociated HMDS due to the shorter diffusion length to the substrate.

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1. Introduction

Most polymer-based flexible substrates are vulnerable to environmental factors such as oxygen, moisture, scratches, etc., because of the softness of the material and the diffusion of the vapor through the substrate film during the exposure to atmosphere. Especially, the high permeability of polymer substrates to oxidizing gases such as O_2 and H_2O can also corrode the metallic electrodes of the electronic devices, such as organic light emitting diodes (OLEDs), organic thin film transistors (OTFTs) device, etc., and can degrade device performance [1,2]. To protect the flexible displays from the atmosphere, a thin-film diffusion barrier composed of a single inorganic layer or a multilayer (a multiple-layer thin film composed of alternate organic layers and inorganic layers) should be deposited both on the flexible substrate and on the surface of the electronic devices as studied by various researchers [3–5]. So, various physical- and chemical vapor deposition methods, such as low-pressure plasma-enhanced chemical vapor deposition (LP-PECVD) [6], atmospheric pressure PECVD (AP-PECVD) [7], atomic layer deposition (ALD) [8], sputter deposition [9], etc., have been studied by many researchers.

Recently, AP-PECVD, especially dielectric barrier discharges (DBDs), has been investigated as one of the methods that could deposit materials at a low cost of ownership because it does not require the use of an expensive vacuum processing system and rather, can adopt in-line processing or roll-to-toll processing easily because there is no need of a loadlock system [10,11]. However, the substrate can be easily damaged by the formation of a filamentary discharge in DBD system, especially at a high-power condition for a high-rate deposition or with a high oxygen content to deposit more stoichiometric SiO_2 [12–14]. To remove possible damage to the substrate by the filamentary discharge, in our previous research [15], the AP-PECVD has been operated with a remote-type configuration by locating the substrate on a third electrode separately from the DBD source during the deposition of SiO_2 thin film, however, this process shows other problems, such as a lower deposition rate, porous film property, etc.

Therefore, in this study, a double-discharge DBD system that is composed of a normal remote-type DBD source and a direct-type DBD has been used to deposit SiO_2 at a low temperature to investigate the possibility of depositing SiO_2 at a higher rate without forming a filamentary discharge. Especially, the effect of the additional direct-type DBD during the operation of the remote-type DBD with different gas mixtures composed of hexamethyldisilazane (HMDS)/O_2/He/Ar on the characteristics of SiO_2 thin film has been investigated as a possible application to thin-film diffusion barriers for flexible electronic devices and substrates.

2. Experimental details

In this study, double discharge system is used for the deposition of SiO_2-like thin film (SiO_X). The double discharge system was composed of a remote-type DBD source and a direct-type DBD source. The remote-type DBD source was located on the top portion of the system, and it consisted of three flat metal electrodes covered with a 3-mm-thick ceramic plate, and the gaps between the electrodes were about 1.5 mm. The ground electrode was

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located at the center of the source, while the two powered electrodes were located at the outside of the ground electrode for the formation of two parallel remote-type DBDs. Another electrode covered with a 1-mm-thick quartz plate, was located 1.5 mm below the remote-type DBD for the formation of a separate direct-type DBD during the operation of the remote-type DBD.

Silicon wafers were used as the substrate and, 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 (~100–500 sccm)/O_2 (~10,000–20,000 sccm)/He (5000 sccm)/Ar (3000 sccm) was used to deposit the SiO_2 thin films, where the mixture of He/Ar was used as the discharge gas, and O_2 was used for the oxidation of HMDS. The remote-type DBDs were generated by applying 7 kV AC power (30 kHz) to the two outside electrodes while the center electrode is grounded. The substrate electrode located below the remote-type DBDs was grounded or was connected to 5 kV AC power (20 kHz) supply for the generation of a separate direct-type DBD. The substrate temperature was maintained below 50 °C using a chiller. During the deposition, the silicon substrates exposed to the plasma were moved at the speed of 0.3 m/scan.

After the deposition of the SiO_X by scanning through the AP-PECVD system, the thickness of the deposited SiO_X thin film was measured using a step profilometer (Tencor, Alpha step 500). The chemical composition of the deposited SiO_X thin film was measured by X-ray photoelectron spectroscopy (XPS; Thermo Electronics, Multilab ESCA2000), Optical emission intensities of the species emitted from the plasma just above the substrate with/without the direct-type DBD during the operation of the remote-type DBD were measured using optical emission spectroscopy (SC-Technology, PCM 420).

3. Results and discussion

Fig. 1 shows the deposition rate of SiO_X thin film measured as a function of HMDS and oxygen in the gas mixture of HMDS (*x* sccm)/O_2 (*x* sccm)/He (5000 sccm)/Ar (3000 sccm) while applying 7 kV, (30 kHz) AC power to the remote-type DBD source. The substrate was grounded or was connected to 5 kV (20 kHz) AC power to form a separate direct-type DBD. As shown in the figure, the increase of HMDS flow rate from 100 to 500 sccm increased the deposition rate of SiO_X thin film from 14 to 38 nm/scan for the ground substrate, while it increased from 18 to 62 nm/scan for the substrate with the direct-type DBD. And the increase of O_2 gas flow rate from 10 to 20 slm decreased the deposition rate of SiO_X thin film almost linearly from 66 to 47 nm/scan for the ground substrate and from 82 to 58 nm/scan for the substrate with the direct-type DBD. Therefore, the increase of HMDS flow rate increased the deposition rate of SiO_X thin film almost continuously for both cases with and without the direct-type DBD above the substrate, however, the substrate with the direct-type DBD showed the higher deposition rate. The increase of deposition rate of SiO_X thin film with the increase of HMDS flow rate is related to the increase of silicon source in the gas mixture. And the decrease of deposition rate with the increase of oxygen flow rate is believed to be related to the decrease of the HMDS percentage in the gas mixture with the increase of oxygen flow rate in addition to the decrease of plasma density with the increase of oxygen flow rate because of the high electron affinity of oxygen atoms. However, the further increase of SiO_X thin-film deposition rate with the additional direct-type DBD above the substrate appears to be related to the additional dissociation of the molecules near the substrate by the additional power absorption just above the substrate through the additional discharge. Therefore, the deposition condition with the direct-type DBD showed the higher deposition rate compared to the condition with the ground substrate.

Figs. 2 and 3 show the atomic percentages of the SiO_X thin films deposited with the conditions in Fig. 1 measured by XPS. As shown in the Fig. 2, for the grounded substrate, with the increase of HMDS flow rate from 100 to 500 sccm, the silicon percentage is not significantly changed (25–27%), while the carbon percentage was increased from 4.1% to 13.1%, and the oxygen percentage was decreased from 69.7% to 61.9%. For the SiO_X thin film deposited with the direct-type DBD, with the increase of HMDS flow rate from 100 to 500 sccm, the silicon percentage is not significantly changed (26.3–27%) too, while the carbon percentage was increased from 1.5% to 9.3%, and oxygen percentage was decreased from 71.7% to 64.5%. Therefore, the SiO_X thin films deposited on the substrate with the direct-type DBD showed similar trends as the SiO_X thin film deposited on the grounded substrate but, for all the HMDS flow rates, the oxygen percentage was higher and the carbon percentage was lower. Fig. 3 shows the effect of oxygen flow rate in the gas mixture of HMDS (400 sccm)/O_2 (*x* sccm)/He (5000 sccm)/Ar (3000 sccm) on the change of atomic percentage of the deposited SiO_X thin film measured by XPS for with and without the direct-type DBD on the substrate. The deposition conditions are the same as those in Fig. 1. As shown in the figure, the change of oxygen flow rate from 10,000 to 20,000 sccm did not change the silicon percentage significantly, and it remained in the range of

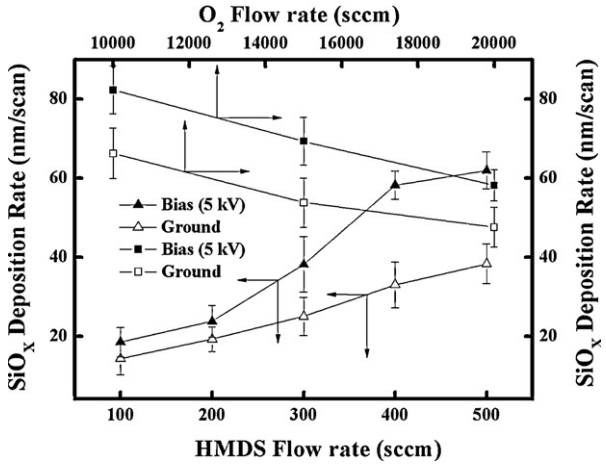

Fig. 1. Deposition rate of SiO_X thin film as a function of the HMDS and O_2 flow rate in the gas mixture of HMDS(varied)/O_2(varied)/He (5000 sccm)/Ar (3000 sccm) and at the applied voltage of 7 kV (30 kHz) to the remote-type DBD. The substrate was grounded or connected to the direct-type DBD of 5 kV (20 kHz).

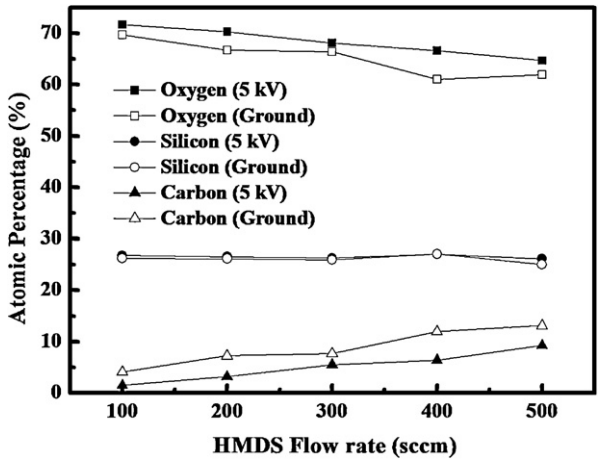

Fig. 2. Atomic percentages measured by XPS in the SiO_X thin film deposited as a function of HMDS flow rate with the conditions.

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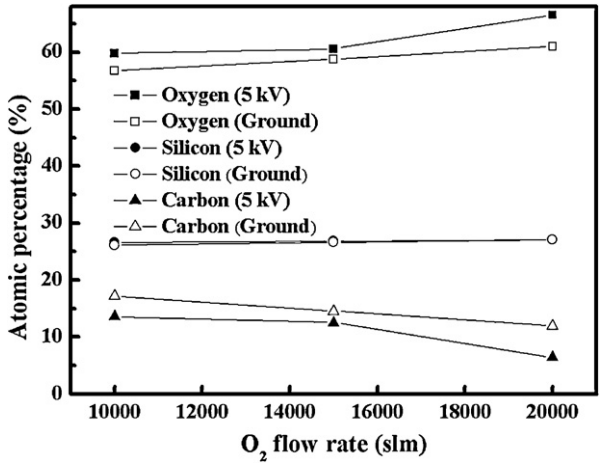

Fig. 3. Atomic percentages measured by XPS in the SiO_X thin film deposited as a function of oxygen flow rate with the conditions.

~26–27% for both cases with and without the direct-type DBD. However, the increase of the oxygen flow rate from 10,000 to 20,000 sccm decreased the carbon percentage from 17% to 12% while increasing the oxygen percentage from 56% to 61% for the grounded substrate. In the case with the direct-type DBD, the carbon percentage was decreased from 14% to 6% while increasing the oxygen percentage from 60% to 66% with the increase of the oxygen flow rate from 10,000 to 20,000 sccm. Therefore, even though the increase of the oxygen gas flow rate in the gas mixture decreased the deposition rate of SiO_X thin film as shown in Fig. 3, the impurity in the deposited SiO_X thin film, such as the carbon percentage in the film, was decreased with the increase of the oxygen flow rate in the gas mixture in addition to the increase of the oxygen percentage for both cases with and without the direct-type DBD because of the increased oxidation of the dissociated HMDS deposited in the SiO_X thin film. In addition, the higher oxygen percentage obtained with the application of the direct-type DBD in addition to a higher deposition rate is believed to be from the further dissociation of gas molecules including oxygen molecules just above the substrate.

Fig. 4 shows the hardness of the SiO_X thin film deposited as a function of O_2 flow rate from 10,000 to 20,000 sccm, and the substrate was connected with ground or applied by using AC power supply with 5 kV (20 kHz) AC power. The SiO_X deposition

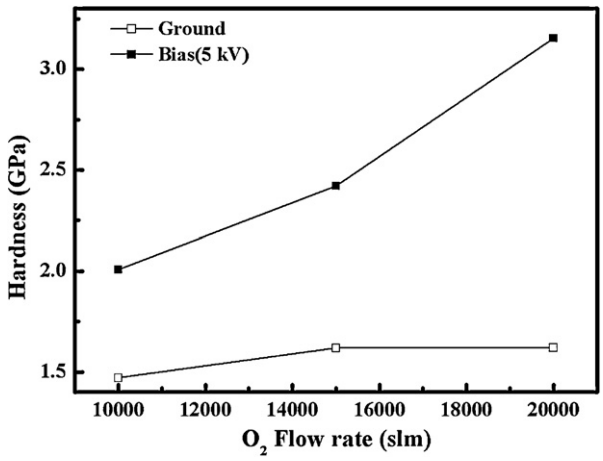

Fig. 4. Hardness measured as a function of O_2 gas flow rate with or without addition of AC-biasing to the subsstrate. The thickness of the deposited SiO_X was maintained at 200 nm. The other conditions were the same as those shown in Fig. 3.

conditions are the same as those in Fig. 1. The hardness of SiO_X is strongly dependent on the SiO_X density. The thickness of the deposited SiO_X thin film was maintained at 200 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 the thin film through the relationship between the load and the displacement into the film. The stabilized hardness value was the lowest at about 1.47 GPa for the SiO_X deposited while grounding the substrate, and the O_2 flow rate was 10,000 sccm. The increase of the O_2 flow rate generally increased the hardness of the deposited SiO_X thin film up to 3.15 GPa for the thin film deposited with 5 kV of AC-biasing. The improvement of SiO_X hardness is related to the increase of SiO_X density and the increase of SiO_X thin-film density with the increasing the O_2 gas flow rate due to the removal of the bondings in SiO_X thin film such as $-(CH_3)_X$ in HMDS. These bondings ($-(CH_3)_X$) tend to show porosity in the film. Increasing the film density can be also partially related to the AC-biasing, because the AC-biasing to the substrate additionally improved the dissociation efficiency of gas molecules (HMDS). As more Si and Oxygen radicals are generated with AC-biasing, more Si–O bond is generated in deposited SiO_X thin film. The improvement of hardness with the increasing of O_2 flow rate and the addition 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 a sheath holding the electric field with the distance larger than a few tens of micrometers exists during the operation of AC-biasing.

4. Conclusions

In this study, the effects of gas combination and double discharge on the characteristics of the SiO_X thin film were investigated using a gas mixture of $HMDS/O_2/He/Ar$. The increase of HMDS flow rate at a fixed oxygen flow rate increased the SiO_X-thin-film deposition rate; however, the deposited SiO_X thin film contained more impurities, such as carbon and hydrogen due to the incorporation of less dissociated/oxidized HMDS in the film. The increase of oxygen flow rate at a fixed HMDS flow rate improved the stoichiometry of the deposited SiO_X thin film because of the enhanced oxidation of the HMDS, but the deposition rate was decreased with the increase of oxygen flow rate possibly due to the decrease of plasma density. The increase of SiO_X-thin-film deposition rate together with the improvement of the stoichiometry of the deposited SiO_X thin film could be obtained by forming an additional discharge area by applying the bias to the substrate. The addition of AC-bias voltage to the substrate also improves the mechanical density of the deposited SiO_X thin film. These results were 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. The use of additional direct-type DBD just above the substrate in addition to the remote-type DBD increased the dissociation of the gas molecules, such as the HMDS and oxygen molecules, further just above the substrate without recombination of the dissociated species in the gas phase, and which appeared to improve both the deposition rate and the stoichiometry of the deposited SiO_X thin film.

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