SF_6 and O_2 Effects on PR Ashing in N_2 Atmospheric Dielectric Barrier Discharge

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Photo Resist (PR) ashing process was carried out with the atmospheric pressure - dielectric barrier discharge (ADBD) using $SF_6/N_2/O_2$. Ashing rate (AR) was sensitive to the mixing ratio of the oxygen and nitrogen of the blower type of ADBD asher. The maximum AR of 5000 Å/min was achieved at 2 % of oxygen in the N_2 plasma. With increasing the oxygen concentration to more than 2 % in the N_2 plasma, the discharge becomes weak due to the high electron affinity of oxygen, resulting in the decrease of AR. When adding 0.5 % of SF_6 to O_2 / N_2 mixed plasma, the PR AR increased drastically to 9000 Å/min and the ashed surface of PR was smoother compared to the processed surface without SF_6. Carbon Fluorinated polymer may passivate the PR surface. It was also observed that the glass surface was not damaged by the fluorine.

Keywords : Dielectric barrier discharge, PR ashing

1. INTRODUCTION

With increasing the size of the flat panel display such as TFT-LCD, the processing area of the glass increases drastically, requiring the large scale of the system for sputtering, ashing and etching processes, respectively. Since most processes for manufacturing the TFT-LCD has been carried out in the vacuum system, the expensive vacuum components become a serious burden on the development of the process system. Two solutions for scaling-up of the process system may be expected: One is to use the wet process based on the chemical reactions and the alternate one uses the dry process which is operated at the atmospheric pressure, respectively. Wet system has an advantage of the expandability of the system volume, however the high cost of chemicals and environmental problem should be considered seriously. For example, the wet process may be carried out with the toxic chemicals like the HF and HCl based solutions[1] for the photo-resistor ashing (or stripping).

Here it is concerned the dry system operated in the atmospheric pressure. The dry processes without high vacuum components have been proposed[2,3] using the corona discharge[4], the plasma jet, the capillary electrode discharge (CED), the microwave discharge, the hollow cathode discharge, and the dielectric barrier discharge[5], respectively. The Corona discharge and plasma jet are not suitable for the practical processes because of provoking the serious thermal damages on the glass. The CED and microwave discharge and the hollow cathode discharges are difficult to expand the discharge volume as large as the process area due to their structural configurations so that they may be suitable to the localized process. The dielectric barrier discharge (DBD) at atmospheric pressure becomes very attractive in the development a large scale of process reactor because the DBD has the many advantages such as no requirement of expensive high vacuum components and non-thermal behavior at atmospheric pressure. Unlikely in the low-pressure plasma process, the processes using DBD are carried out by the radicals and UVs which are produced in the discharge.

The properties of discharge and process are considered simultaneously to figure out the characteristics of the system, which play an important role in the development of the process system. Because the ashing process of photoresistor on the glass is the large scale of the process in the semiconductor or TFT-LCD fabrications, this study is focused on the development of the asher using DBD. The characteristics of DBD have been investigated with the operating frequency and the reactor capacitance, obtaining the design rule of DBD process reactor[6]. The DBD process has been carried out using various system configurations such as the pin-type electrode system[5], the metal electrode system[7], the system using the RF power[8], the system of processing between the electrodes[9], and the blower system[10], respectively. These studies had normally achieved the ashing rates (AR) of 2000 ~ 3000 Å/min. For DBD using RF power, it has been reported that AR is a little higher but the ignition of DBD is difficult[8]. In practices, higher AR is required as over than 5000 Å/min.

In the DBD asher, it is issued on the high AR so that the PR ashing using the blower type DBD was investigated with various gas mixtures and operating conditions. The measurement of discharge properties were monitored by electrical and optical probes, and the surface morphology was observed with considering the discharges.

2. EXPERIMENTAL SETUP

Figure 1 shows the blow type of dielectric barrier discharge system (DBD) for PR ashing[10]. As shown in the Fig. 1, the mixed gas was delivered to the top of the DBD chamber and the discharge plasma was generated in the bottom region of the chamber. The bottom region of the chamber consisted of upper and lower electrodes which were made of the one side metal coated alumina (Al_2O_3) having the thickness of 1 mm. Power (frequency of 15 kHz and voltage of 6.4 kV in RMS value) was delivered to the metal part of the electrode. The gap distance between two electrodes was approximately 1 mm and the discharge took place between the electrodes. Since the bottom electrode of the chamber had many holes with diameter of 0.8 mm, the discharged gas was allowed to be extracted through the holes. Due to very short collision mean free path, the order of a few micrometers, the charged particles were quickly recombined just after extraction. Thus the radicals could conduct reactions in the blow type DBD asher, which might prevent arc or the charge damages on the substrate.

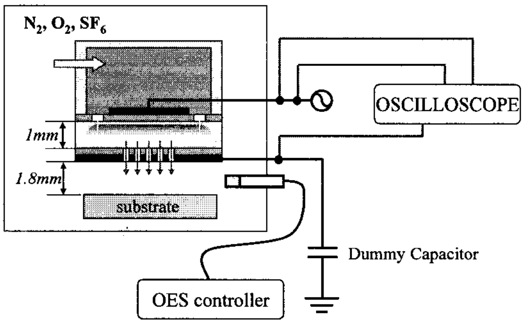

Fig. 1. System Schematic diagram of the blow type of DBD asher.

Figure 2 shows the glass substrate which was coated with 3000 Å-height of amorphous silicon (a:Si) and 3 μm of PR patterns on the a:Si. The gap distance between PR patterns was 100 μm and the thickness of PR pattern was 4.5 μm. The test coupon size was 3 cm x 3 cm glass, which was located at 1.8 mm beneath the reactor. Oxygen and sulfur hexafluoride with nitrogen basis were mixed, delivering in the discharge region of the DBD blower. Process was carried out for 30 seconds. Total flow rate was fixed to 100 lpm. O_2 flow rate varied from 0 to 3 lpm and SF_6 flow rate varied from 0 to 1 lpm. Input voltage and discharge current were measured by the high voltage probe and the current probe. The serial capacitor of the reactor was employed to measure the charge quantity of the DBD. The dissipated power could be monitored using the discharge voltage, current, and charges. Optical emission spectroscopy was focused at the extraction hole of the lower electrode measure the vibrational and rotational temperatures of nitrogen radicals, and also monitored the species in the discharge [11,13]. Ellipsometry and scanning electron microscopy (SEM) are employed to study the AR and surface morphology.

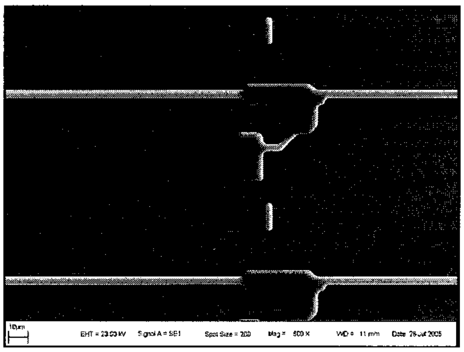

Fig. 2. SEM image of test substrate glass which is covered with 3000 Å-height a:Si and 3 μm PR patterned on the a:Si.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Oxygen atom reacts effectively with carbon and hydrogen of PR, becoming the main ashing gas for PR ashing. Discharge properties are observed with various oxygen concentrations in the nitrogen based DBD. As shown in Fig. 3, the discharge voltage increases as the partial pressure of oxygen increases. Because the affinity of oxygen is high to generate the electronegative plasma easily, more energetic electrons are required to sustain the discharge in oxygen plasma, resulting in the requirement of higher breakdown voltage compared to that of the electropositive gases[12]. In general, only small

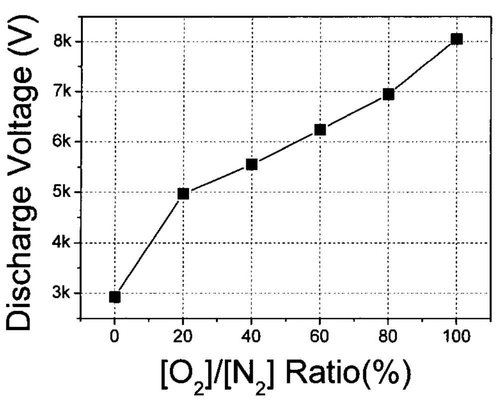

Fig. 3. Discharge voltage with the ratio of O_2 and N_2. Electronegative O_2 gas requires stronger electric field to sustain the breakdown.

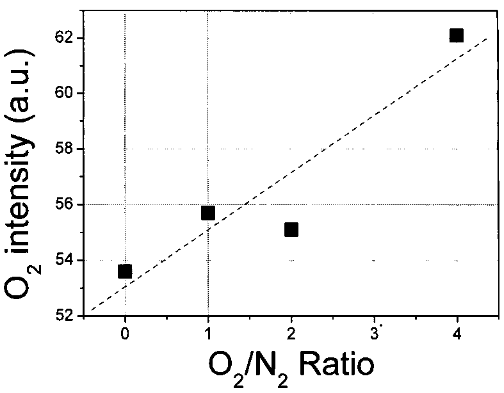

Fig. 4. O_2 intensity with various oxygen concentrations in the nitrogen plasma. Dotted line represents to the linear fitted result.

amount of oxygen is added in the nitrogen DBD asher because the discharge power efficiency in high oxygen concentration may not appropriate to the practical system. The ratio of oxygen to nitrogen is chosen less than 10 % in the following experiments.

Ashing of PR is preceded dominantly by the oxygen radical, whose production is sensitive to the discharge property, especially the oxygen radical density and temperature of the electrons in the DBD. Under the assumption that the production of oxygen radical is proportional to the excitation of oxygen molecule through the electron collision, the oxygen intensity from OES spectrum is observed with various oxygen concentrations in the nitrogen based DBD. The results are shown in Fig. 4. As indicated by the fitted line, the O_2 intensity is linearly increased with the oxygen concentration. At 2 % of oxygen in nitrogen DBD, it is noted that the O_2 intensity is slightly lower from the fitted value. It implies that the O_2 may be dissociated effectively to [O], resulting in the lower intensity of oxygen molecule.

In the atmospheric pressure, the electron temperature (T_e) is extremely difficult to measure using an electrical probe because mean free path of electron is short. So the emission spectroscopy is used to diagnose T_e[13-15]. Atmospheric low-temperature plasma is classified to the state of tow temperature local thermodynamic equilibrium (2T LTE) and temperatures are as follows in 2T LTE[16]

$$T_e \geq T_{exc} \approx T_{vib} \approx T_{ion} \gg T_{rot} \approx T_{tran} \tag{1}$$

where T_{exc} is excitation temperature, T_{vib} is vibration temperature, T_{ion} ion temperature, T_{rot} is rotation temperature, and T_{tran} is translation temperature.

Using equation (1), T_e is calculated from T_{vib} indirectly and the gas temperature is calculated from T_{rot}. Band intensities in emission is as follows[17]

$$I_{em.}^{v'v''} = \frac{64\pi^4 hc^2 R_e^2 (v_{n''v''J''}^{n'v'J'})^4 q_{v'v''}}{3} \frac{S_J B_v}{kT_{rot}} N_{n'} \times \exp\left[-\frac{1}{k}\left(\frac{G_v(n',v')}{T_{vib}} + \frac{F_r(n',v',J')}{T_{rot}}\right)\right] \tag{2}$$

where h is Planck's constant, c is velocity of light, R_e is electronic translation moment, $q_{v'v''}$ is Franck Condon factor, S_J is line strength factor, J is quantum number for rotation energy level , v is quantum number for vibration energy level, B_v and F_r is the rotation energy constant, and G_v is vibration energy constant.

Plasma emission spectrum is obtained using eq. (2) as a Dirac impulse. After that, it is calculated with considering broadening effect as follows

$$G(\lambda_0) = \frac{2}{\Delta\sqrt{\pi}} \exp\left(-\frac{(\lambda-\lambda_0)^2}{(\Delta/2)^2}\right) \tag{3}$$

where Δ represents the full width at 1/e of the maximum located at the wavelength λ_0[15]. By Comparing experiment OES result with simulated Gaussian profile which is acquired using eq. (3), the vibration temperature and rotation temperature was measured. In this study, the temperature of nitrogen molecules is observed using nitrogen molecule spectrum ($C^3\Pi_u$) from OES data[13]. In Fig. 5, the temperature of nitrogen molecules are observed with varying the oxygen concentrations in the nitrogen based DBD. Rotational temperature of nitrogen is insensitive to the oxygen concentration and, however the vibrational temperature drastically decreases at the oxygen concentration of 1 % and then increases at 3 % in O_2/ N_2

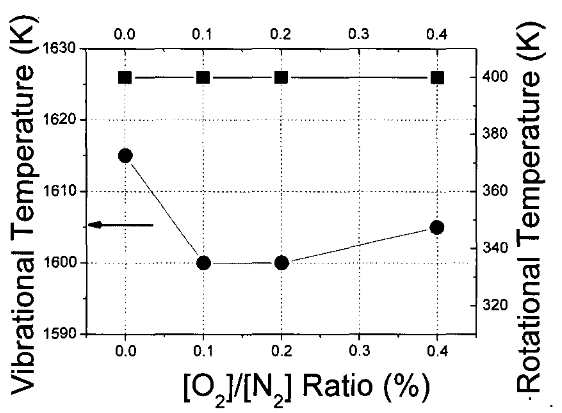

Fig. 5. Vibration and rotation temperatures of N_2 ($C^3\Pi u$) radical with various O_2 concentration to the nitrogen.

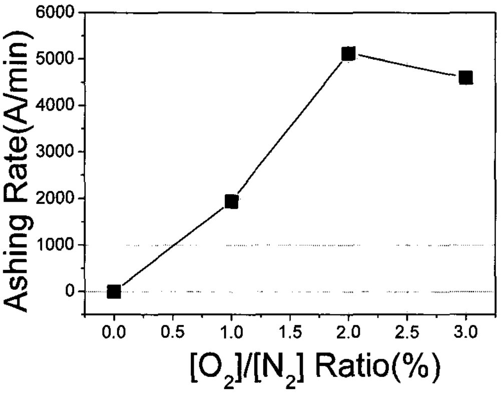

Fig. 6. Ashing rates with various O_2 concentrations in the nitrogen based DBD. Ashing rate has a maximum value at 2 % of oxygen concentration.

respectively. In general, the nitrogen temperature decreases with increasing the oxygen concentration. It implies that the nitrogen energy is transferred to the oxygen molecules effectively. Furthermore, Figs. 4-5 show that nitrogen affects the generation of the oxygen radicals at a specific mixing ratio, 2 % of O_2 in N_2 based DBD.

Figure 6 shows the AR of PR is observed with increasing the oxygen concentration of 1- 3 % in N_2 based DBD. AR has the maximum value at the oxygen concentration of 2 %. Most ashing process is carried out by the oxygen radical reaction with the hydrogen and carbon atoms in PR which produce the volatile molecules of CO_2 and H_2O, respectively. Therefore, from Figs. 4-6, the oxygen radical is produced effectively at 2 % of oxygen in the nitrogen based DBD, achieving the highest AR.

Discharge current is as follows[20]

$$I_{discharge} = A\left(nqv + C\frac{dV}{dt}\right) \tag{4}$$

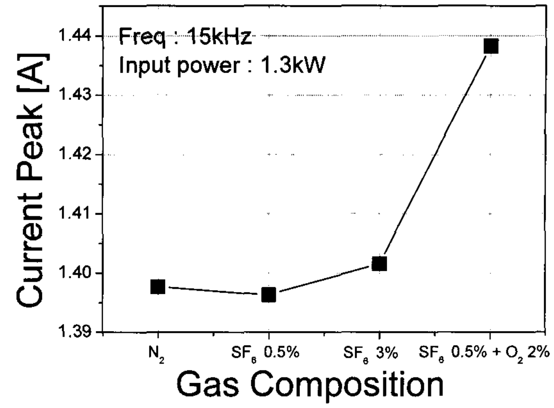

Fig. 7. Discharge current with various gas combinations, N_2 (100 %), SF_6 (0.5 %)/ N_2 (99.5 %), SF_6 (3 %)/ N_2 (97 %) and SF_6 (0.5 %)/ O_2 (2 %)/ N_2 (97.5 %), respectively. The discharge current is maximized at SF_6 (0.5 %)/ O_2 (2 %)/ N_2 (97.5 %).

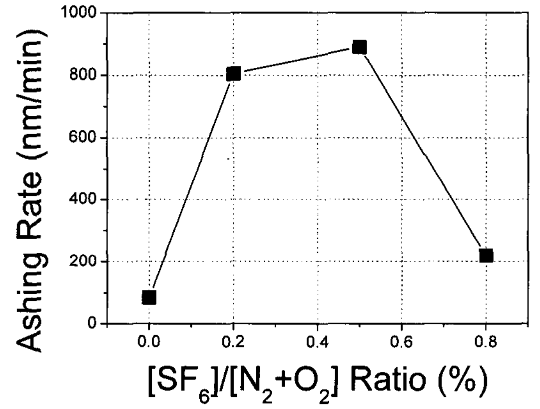

Fig. 8. Addition of SF_6 in O_2+N_2 DBD increases the ashing rate. The highest ashing rate of 9000 Å/min is achieved at 0.5 % of SF_6.

where A is the electrode area, n is the discharge density, q and v is charge and velocity respectively, C is the capacitance of dielectric, and V is the applied voltage. As seen from eq. 4, the discharge current increases in accordance with the increase in the discharge density. And O radicals which strip the PR are generated more as discharge current is increased. Discharge current is affected by the gas combination. Fig. 7 shows the dissipated current with various gas mixtures as N_2 (the concentration of 100 %), SF_6(0.5 %)/ N_2(99.5 %), SF_6(3 %)/ N_2(97 %) and SF_6(0.5 %)/O_2(2 %)/ N_2(97.5 %), respectively. The current data were obtained from the peak value of the discharge current signal. When introducing SF_6 in nitrogen DBD, the discharge current tends to decrease due to generation of the electronegative SF_6 plasma which has the stronger electron

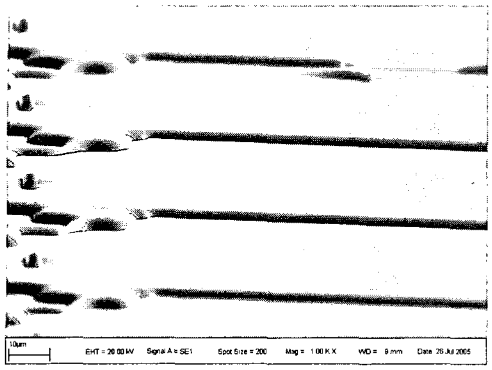

Fig. 9. SEM image of the ashed glass substrate patterned PR. No serious damage on glass by the fluorine and the smooth surface are observed.

affinity (1.070±0.070 eV[18]) than that of oxygen (0.4480±0.0060 eV[19]), requiring the higher electric field. However, for the mixture of $SF_6/O_2/N_2$, the discharge current increases drastically, which is expected to improve the AR. For the high discharge current, it is postulated that the radicals of oxygen and fluorine produced and ionized by some reasons effectively. This hypothesis may be confirmed by the measurement of fluorine and oxygen using the mass spectroscopy in future.

Figure 8 shows the results of the AR with varying the concentration of SF_6 in O_2+N_2 DBD. As shown in Fig. 7, the discharge current is enhanced by the addition of SF_6 in O_2+N_2 DBD. As expected in Fig. 7, the oxygen and fluorine radicals are effectively generated and reacted with the hydrogen and carbon in PR, consequently increasing the AR with SF_6 in O_2+N_2 based plasma. When increasing the concentration of SF_6 up to 0.5 %, it is achieved the highest AR of 9000 Å/min. At the 0.8 % of SF_6, AR decreases because the discharge is reduced by the generation of the electronegative property of SF_6 plasma. Ashed surface of PR is smoother compared to the processed surface without SF_6 as shown in the SEM image of the ashed glass substrate shown in Fig. 9. Fluorine from SF_6 may generate the CF_n polymer which works as the passivation material[2], resulting that the PR pattern is ashed in good shape having the smoother surface. Also Fig. 9 reveals no serious damage on the glass surface by the fluorine.

4. CONCLUSION

In this study, PR ashing process is performed using the blower type of atmospheric dielectric barrier discharge (DBD). Major ashing processes are carried out through the reaction of oxygen radicals with the hydrogen and carbon atoms in PR, producing the volatile molecules of CO_2 and H_2O. The AR has a maximum value (5000 Å/min) at the oxygen concentration of 2 % in nitrogen based DBD where the oxygen radical was generated effectively. When SF_6 of 0.5 % was added to O_2+N_2 based DBD, the discharge current and AR increased drastically to 9000 Å/min. Discharging mechanism is not understood clearly at this moment, however the fluorine dissociated from SF_6 seems to play an important role in the high AR through the generation of the volatile CF_4 form, so that PR is stripped effectively. Consequently the gas mixing ratio is important in improving the PR AR. With small amount of SF_6, AR improves drastically. The production of CF_n polymer on the surface due to the fluorine of SF_6 may improve the protection of the pattern and surface damage on the glass surface.

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