Damage-Free Treatment of ITO Films using Nitrogen-Oxygen (N_2-O_2) Molecular DC Plasma

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ABSTRACT: In this study, the surface of ITO films was modified using N_2-O_2 molecular plasma, and the effects of oxygen concentration in the plasma on the ITO surface properties were investigated. Upon plasma treatment of ITO films, the surface roughness of ITO films seldom changed up to the oxygen concentration in the range of 0% to 40%, while the roughness of the films slightly changed at or above the oxygen concentration of 60%. The contact angle of water droplet on ITO films dramatically changed with varying oxygen concentration in the plasma, and the minimum value was found to be at the oxygen concentration of 20%. The plasma resistance at this condition exhibited a maximum value, and the change of resistance showed an inverse relationship compared to that of contact angle. From these results, it was conjectured that the chemical reactions in the sheath of the molecular plasma dominated more than the physical actions due to energetic ion bombardment, and also the plasma resistance could be used as an indirect indicator to qualitatively diagnosis the state of plasma during the plasma treatment.

Key words: Indium tin oxide (ITO), Molecular plasma, Nitrogen, Oxygen, Surface damage

1. Introduction

Low-temperature plasma is composed of partially ionized atomic or molecular gases, which contain charged particles such as positive (or negative) ions and electrons[1-2]. In the low-temperature plasma, ion bombardments occur in the sheath region, generating highly reactive radicals, thus lowering the reaction temperature[1-4]. Plasma has been typically used in various applications such as plasma chemistry, surface modification, thin film deposition, etching processes, etc.[1-4] One useful application is the surface treatment of substrates using plasma, since the treatment gives rise to chemical and physical modification of the substrate surface without affecting the bulk properties. Plasma treatment may change the surface properties such as wettability, adhesion strength, barrier protection property and bio-compatibility[2-4]. Ion bombardment in the plasma treatment plays an important role not only to break chemical bonds at the surface of materials but also to form the surface radicals. Plasma treatment using reactive gases can generate chemically different radicals at the surface, and the surface property can be changed to either hydrophilic or hydrophobic upon the exposure to the reactive plasma. In spite of the various advantages of plasma treatment, problems still remain with the surface treatments using plasma. Most of all, the surface damages due to energetic ion bombardments could seriously affect the properties of films. Thus, it is important to find optimum condition in that surface damages can be minimized and surface activations can be effectively carried out.

In this study, the plasma with the mixture of N_2 and O_2 was used to modify the surface properties of indium tin oxide (ITO) thin films without causing significant surface damages. This approach is related to reduce the energy of ion bombardment through the sheath using the difference between atomic and molecular plasma. In addition, the effects of the mixing ratio of N_2 to O_2 gases were investigated to find the optimum condition for damage-free surface activation.

2. Experimental Details

ITO films were plasma-treated using a gaseous mixture of O_2 and N_2, and effects of O_2 concentration were investigated. The plasma was generated by a direct current (DC) power source. The diameter of electrodes was 10 cm, and the electrode gap was 4 cm. The applied power and plasma treatment time were kept at 30 W and 20 min, respectively. A reaction chamber was evacuated by a mechanical pump up to a base pressure of 5×10^{-3} Torr, and

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the working pressure was maintained at 600 mTorr during the plasma treatment. Chamber pressure was monitored by a convector gage (Granville-Phillips), and the ratio of $[O_2]/[N_2+O_2]$ was ranged from 0% to 100%. The detailed experimental conditions for the plasma treatment of ITO films is listed in Table 1.

Optical emission spectra of plasma discharge using O_2/N_2 gas mixtures were measured by a photodiode array spectrometer (Oceanoptics S2000). The electric properties of plasma were measured using a multimeter (Keithley 2000), and the plasma resistance was calculated using current-voltage characteristics. Surface morphology of plasma-treated ITO films was measured by an atomic force microscopy (AFM, Digital Instruments NanoScope IIIa), and the sheet resistance of the films was analyzed by a 4-point probe system. The surface properties of ITO films were studied by a contact angle meter (Surfacetech GSS), and the surface energy was evaluated using the results from contact angle measurements.

3. Results and Discussion

Fig. 1(a) shows the breakdown voltage of N_2-O_2 plasma according to the mixing ratio of N_2/O_2 gases. The breakdown voltage increased with the increase of oxygen concentration. This could be explained that the oxygen, as an electron-negative gas in the plasma, enhances the electron attachment process at the initial stage of discharge[4)], and this prevents from the initial breakdown process. Fig. 1(b) shows the discharge resistance of N_2-O_2 plasma according to the mixing ratio of N_2/O_2 gases. The current-voltage (I-V) curve of the molecular plasma was well obeyed by Ohm's law, and thus the inverse slope of I-V plot can determine the resistance of plasma[5)]. The plasma resistance at the oxygen concentration of 20% reached up to 2.2 kΩ, and then the resistance rapidly decreased with increasing oxygen concentration in the plasma. The main reason for the maximum resistance at the oxygen concentration of 20% could be explained by the production of oxygen radicals in the plasma. The ionization processes at low plasma resistance region were dominated compared to the production of radicals resulting from the decrease of the plasma resistance. Thus, the ratio of $[O_2]$ to $[N_2+O_2]$ played an important role in the collision mechanism between molecules and electrons.

This tendency was in agreement with the results of optical emission spectra from N_2-O_2 plasma. Optical emission spectra and emission intensity of N_2-O_2 molecular plasma according to $[O_2]/[N_2+O_2]$ ratio are shown in Fig. 2 and Fig. 3, respectively.

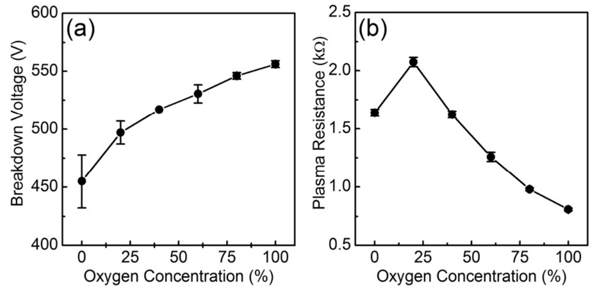

Fig. 1. Electrical properties of N_2-O_2 molecular plasma according to oxygen concentration; (a) breakdown voltage and (b) plasma resistance

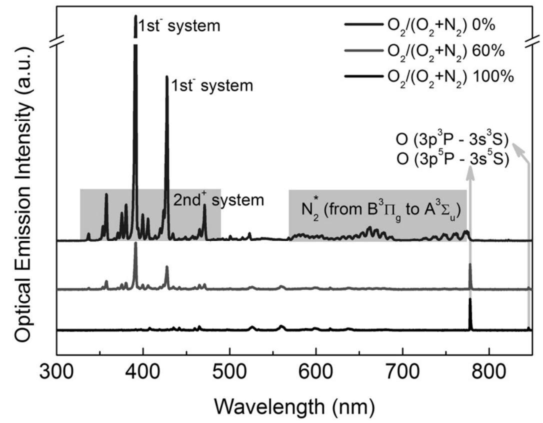

Fig. 2. Emission spectra of N_2-O_2 molecular plasma at different $[O_2]/[O_2+N_2]$ ratio

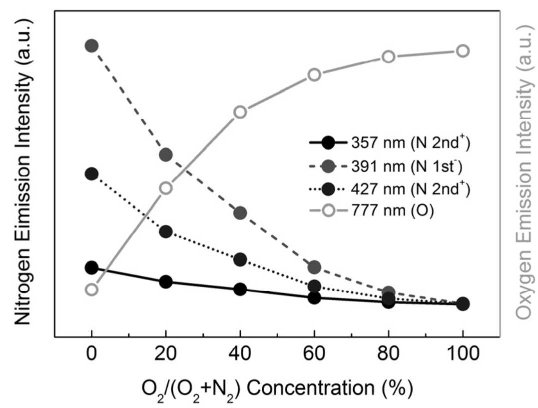

Fig. 3. Emission intensity of N_2-O_2 molecular plasma according to $[O_2]/[O_2+N_2]$ ratio

All emission lines from nitrogen in the N_2-O_2 plasma were assigned as transitions of molecular nitrogen. The 2nd positive lines of N_2 in the range of 300 − 400 nm was attributed to the transition of $C^{3\Pi}{}_u - B^3\Pi_g$, and the 1st negative lines of N_2^+ at 391.4 and 427.8 nm were assigned to the transition of $B^2\Sigma_u^+$ - X^2 Σ_g^+. The 1 positive lines of N_2 in the range of 500 - 800 nm were very weak compared to 2nd positive lines and 1st negative lines. Otherwise, the emission lines from oxygen were dominated by the two atomic lines at 777 and 844 nm, corresponding to the oxygen atom transition $O(3p^5P \rightarrow 3s^5S)$ and $O(3p^3P \rightarrow 3s^3S)$, respectively. The oxygen emission lines rapidly increased up to the oxygen concentration of 40% in the plasma, and then saturated, while the tendency for nitrogen emission lines exhibited an inverse relationship. Especially, the fast changes of emission intensity occurred at the oxygen concentration of 20% in the plasma, and it was closely related to electrical properties of N_2-O_2 molecular plasma.

Fig. 4 shows AFM images and roughness of ITO films according to oxygen concentration in N_2-O_2 molecular plasma. The surface roughness of ITO films seldom changed with increasing oxygen concentration in the range of 0% to 40%, while the roughness of the films slightly increased at or above the oxygen concentration of 60%. This implied that surface damages due to energetic ion bombardments in the sheath region were minimized in the molecular plasma, and this can be explained in terms of characteristics of molecular gas plasma. Unlike an atomic plasma, gas molecules in the molecular plasma has inner degrees of freedom, which are related to their vibrational and rotational motion in plasma, and the main portion of an energy input in the molecular plasma was used in the excitation of molecular vibrations. This energy loss could cause to reduce high energy electrons in the plasma and lead to the decrease of energetic ions in the sheath region. From these results, it was conjectured that the chemical reaction due to oxygen related radicals dominated more than the physical actions including ion bombardments. The surface activation of ITO films due to chemical reactions in the sheath region could be verified from a contact angle measurement. Fig. 5 shows contact angle images of liquid droplets on ITO films at different oxygen concentration in the plasma. The distilled water (surface energy = 72.8 mN/m) was used as a liquid droplet, and the contact angle between the ITO and the water droplet was analyzed using an image analysis software (Image J, open-source). The contact angle at the oxygen concentration of 20% in the plasma showed a minimum value. As shown in Fig. 1(b), the plasma resistance in this condition exhibited a maximum value, and the variation tendency showed an inverse relationship compared to that of contact angle. Thus, it was concluded that two values, the plasma resistance and the contact angle, are closely related each other. In addition, the surface energy is an important factor in the surface treatment process, and it is well-known that the contact angle is closely related to the surface energy. The surface energy calculated by a Girifalco-Good-Fowkes-Young method[6)] is given by:

$$\gamma_{SV} = \frac{\gamma_{LV}(1+\cos\theta)^2}{4\pi^2} \tag{1}$$

where γ_{SV} is the surface energy corresponding to solid-liquid interface, γ_{LV} is the surface energy of measuring liquid, and θ is the contact angle between the solid and the measuring liquid. Eq. (1) directly shows the relationship between the surface energy and the contact angle, and the tendency has an inverse relationship in this case.

4. Conclusions

In this study, the surface of ITO films were modified using N_2-O_2 molecular plasma, and the effects of oxygen concentration in the plasma were investigated in detail. After the plasma modifications of ITO films, the surface roughness of ITO films

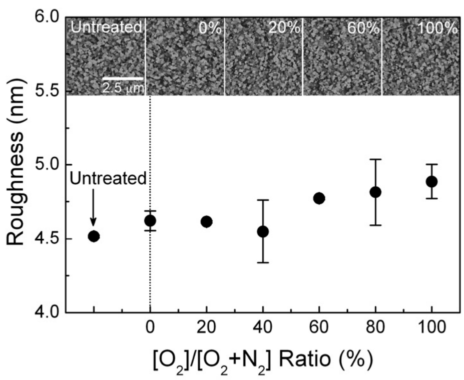

Fig. 4. Roughness (R_{rms}) of ITO films plasma-treated at different $[O_2]/[O_2+N_2]$ ratios (inset: AFM images of ITO films treated at different O_2 concentration)

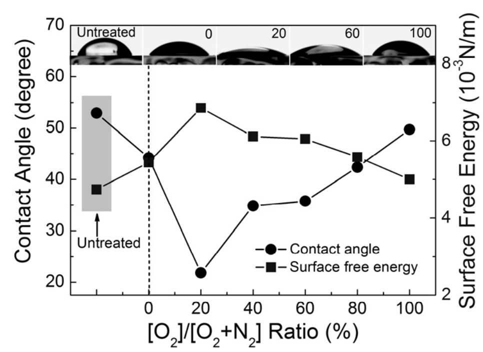

Fig. 5. Contact angle (-●-) and surface energy (-■-) of ITO films plasma-treated at different $[O_2]/[O_2+N_2]$ ratio (inset: contact angle images of distilled water-droplet on ITO films treated at different O_2 concentration)

seldom changed at the oxygen concentration in the range of 0% to 40%, and the roughness of the films slightly changed above the oxygen concentration of 60%. The contact angle of a water droplet on ITO films dramatically changed with varying the oxygen concentration in the plasma, and the minimum value was found at the oxygen concentration of 20%. In addition, the plasma resistance in this condition exhibited a maximum value, and the variation tendency showed an inverse relationship compared to that of contact angle. From these results, it was conjectured that the chemical reactions in the sheath of the molecular plasma dominated more than the physical actions due to energetic ion bombardments, and also the plasma resistance could be used as an indirect indicator to qualitatively monitor the state of plasma during the plasma treatments.

Acknowledgments

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