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Study of Nitrogen Plasma Treatment on Indium Tin Oxide Thin Films

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We studied the effect of nitrogen plasma treatment on the indium-tin-oxide thin films. By monitoring the in-situ optical emission spectra during the capacitively coupled plasma treatments, we investigated the populations and the energies of the nitrogen plasma species. In particular, the nitrogen plasma consisting of excited neutral and ionic molecular species was studied and found to depend on the nitrogen flow. After the nitrogen plasma treatment, the optical band gap of the indium-tin -oxide thin films was reduced, and their resistance was increased. Interestingly, when the energy of the excited neutral molecular series became higher, the band tails increased but the sheet resistance was suppressed. We believe that co-generations of nitrogen doping species and oxygen vacancies by an energetic plasma were responsible for these results.

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I. INTRODUCTION

Indium–tin–oxide (ITO) thin films, a SnO_2 doped In_2O_3, have been widely used as transparent electrodes and hole injection layers in the optoelectronic applications, especially in liquid crystal flat panel displays, solar cells, lighting emitting diodes and so on [1–3]. The ITO is a degenerate n-type semiconductor and its conductivity is originated from the Sn dopings and O vacancies [4]. If one can modify the activation states of Sn and the population of O vacancies, the conduction of ITO can be controlled. For this matter, the plasma treatment has an obvious advantage in the sense of that 1) the surface of as-grown films can be modified without raising the template temperature and 2) an exposure to harmful gas, such as NH_3, NO, CO and so on, can be avoided [5]. With this idea, many works have been reported. Among them, S. Fujita's *et al.* group reported the increase of sheet resistance and work function after O plasma treatment [6–8]. The mixtured O-N plasma treatment on ITO was also studied especially for the organic LED applications to use further improved hole injection capability and durability in the device operations [9].

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It is known that the O states are stabilized and become more resistive when the O vacancies are replaced by N [10,11]. The hole injection and the interfacial adhesion properties can be also improved. However, few research regarding a sole N plasma treatment were presented [12, 13]. Besides the diagnosis in the N plasma states are absent in these works. Please note that the energy and population of the plasma species actually governs the surface reaction process including dopings, structural evolutions and defect generations.

With this in mind, we have investigated the effect of N plasma treatment on ITO films in terms of electrical conductivity and optical properties, along with the study of the plasma dynamics. In particular, we controlled the N plasma by adjusting N flow rate in capacitively coupled plasma (CCP) system and monitored the plasma states by observing the plasma optical emission spectroscopic (OES) methods.

II. EXPERIMENTAL METHODS

The ITO thin film of the glass substrate of 1 × 1 inch was purchased from AMG tech, which was grown at the

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room temperature followed by the post annealing at 300 °C by the sputtering methods. Its thickness is 150 nm and resistivity is < 10^{-3} Ωcm. The nitrogen treatment was conducted by a RF-CCP system (13.56 MHz). The distance between two flat electrodes in CCP was fixed to 20 mm. The used N_2 gas flow rate was 10, 20, 40 and 60 sccm while the power was kept 300 W at the room temperature. Here, we chose the particular power of 300 W because most obvious OES intensity changes were found in the positive series and negative series. The characteristics of the plasma states were identified by a plasma OES in the range of 300 – 900 nm (HORIBA, TRIAX). The morphology of each sample was measured by scanning electron microscope (MIRA3, TESCAN). Optical transmittance was measured by using a UV-visible spectroscopy (Lambda25). The thin film thickness was measured using a Thin Film Thickness Measurement System (ST4000, K-MAC). The sheet resistance was then measured by the 4-probe methods.

III. RESULTS

Figure 1 (a) and (b) show the OES of 300–900 nm obtained during the nitrogen plasma treatment with 300 W of power. Plasma intensity is affected by the electron population at the higher transition levels; $I \propto N \cdot A \cdot hf$, where I is the plasma intensity, N is the electron number density at the upper energy level, A is the Einstein coefficient, and hf is the emission energy. Since the peak position corresponds to the energy difference of the specific transitions, we can predict the population of plasma species by analyzing the intensity of the OES peaks of a certain wavelength [14]. The excited neutral molecular plasma species, which were focused in the current work, are the 1st positive series at 620–690 nm (ν=3; ν=vibration quantum number), 710–790 nm (ν=2), and 840–895 nm (ν=1) as well as the 2nd positive series at 316, 337, 358 and 375 nm. In addition, the 1st negative series of molecular ions used is at 391 nm. Note that the nitrogen atom species were not observed [15–18].

Figure 2 (a – c) present the change in OES intensity dependent on the N_2 flow. Note that the integrated intensity was considered for the first positive series while the peak intensity was used for both the second positive

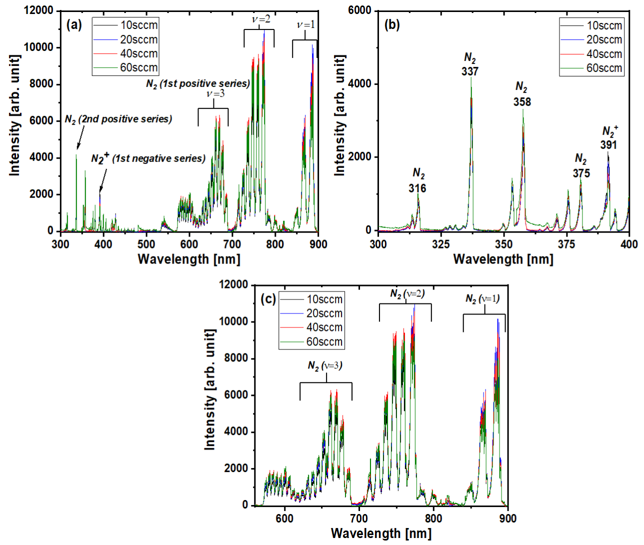

Fig. 1. (Color online) (a) OES of the ITO films with a different N_2 flow, (b) 2nd positive and 1st negative series, (c) 1st positive series.

series (sum of the four peak) and the negative series. The details regarding the OES intensity value of the transitions were summarized in the Table 1. As the N_2 gas flow increases, the OES intensity regarding the 1st positive ($B^3\Pi_g \rightarrow A^3\Sigma_u^+$) series increase by 12% from 10 sccm to 40 sccm and decrease by 5.6% to 60 sccm while the 2nd positive ($C^3\Pi_u \rightarrow B^3\Pi_g$) series gradually increase by 20.1%. Note that incremental rate of the OES intensity for the 2nd positive series is much higher than that of the 1st positive series. Besides, the OES intensity of the 1st negative species ($B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$) decreases by 35.8%. Based on this comparative OES observation of the 1st and 2nd positive series with an assumption of electron energy distribution function as Maxwellian, we can conclude that, as the N_2 flow increases, 1) the average energy of the neutral molecular species become blue-shifted and 2) the energy value having maximum population become beyond the $B^3\Pi_g$ (7.35 eV) level at the N_2 flow of 60 sccm. Please note that 1st negative series are usually responsible for defect generations due to the vigorous reactivity. But considering comparatively high Einstein coefficient of 391 nm peak, 7.6×10^7/s, we can assume that the population of 1st negative series is that high in our work [17].

In order to study the optical properties of the plasma treated ITO thin films, we conducted the UV-VIS measurements. Figure 3 (a,b) show the results of transmittance in the wavelength range from 200 nm to 800 nm

Table 1. Plasma species observed in the OES.

Plasma species	Range (nm)	OES intensity			
		10 sccm	20 sccm	40 sccm	60 sccm
1st positive series $B^3\Pi_g(7.35\ \text{eV}) \rightarrow A^3\Sigma_u^+\ (6.17\ \text{eV})$	620–690 710–790 840–895	9.36×10^6	1.04×10^7	1.06×10^7	1.01×10^7
2nd positive series $C^3\Pi_u\ (11.03\ \text{eV}) \rightarrow B^3\Pi_g\ (7.35\ \text{eV})$	316, 337, 358, 375	3.28×10^3	3.50×10^3	3.90×10^3	4.10×10^3
1st negative series $B^2\Sigma_u^+\ (18.7\ \text{eV}) \rightarrow X^2\Pi_g^+\ (15.6\ \text{eV})$	391	2.16×10^3	1.87×10^3	1.58×10^3	1.39×10^3

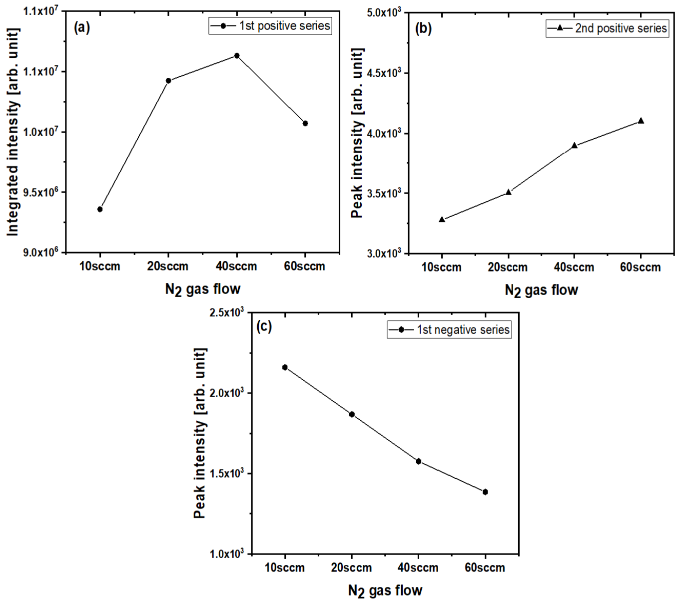

Fig. 2. (a) OES integrated intensity of 1st positive series, (b) 2nd positive series, and (c) 1st negative series.

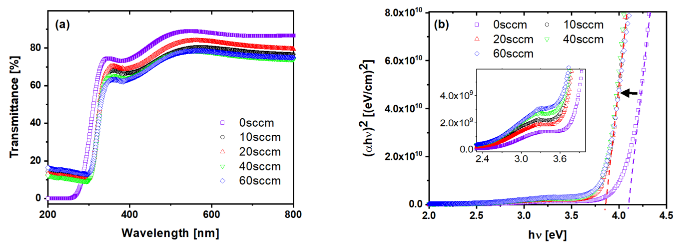

Fig. 3. (Color online) (a) Optical transmittance spectra of ITO films treated with different N_2 flow, (b) Tauc plot for the direct allowed transition of energy gap. Inset: band tails.

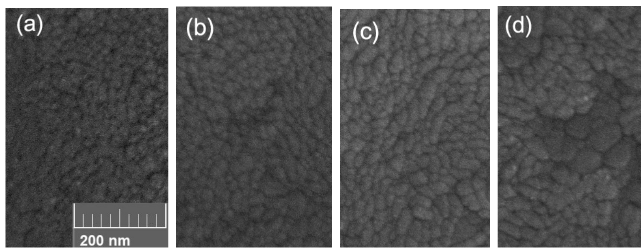

Fig. 4. (Color online) (a-d) Top view of SEM images of the N plasma treated ITO films; (a) N_2 flow of 10 sccm, (b) 20 sccm, (c) 40 sccm, (d) 60 sccm.

and its Tauc plot. With an increase of N_2 flow, the transmittance in the visible region decreases by around 15–17%, which is possibly related to the elevated optical scattering by the defects. Using the Tauc plot with m = 1/2, the direct band gap energy was estimated, which was reduced from 4.2 eV to 3.7–3.8 eV after the plasma treatment. It is known that the valence band maximum energy is shifted higher when N occupy the O vacancies or replace the O [19]. Here, the clear difference between the ITO films was not observed. To investigate the defect populations further, the band tails were monitored as shown in the Fig. 3 (b) inset. We found the increase of the band tail area with an increase of N_2 flow which directly correlated to the transmittance results. Thus, we were able to claim that the excited neutral molecular series having a higher energy results in the optical defects.

The effect of the plasma treatment on the ITO film morphology was studied by SEM measurement [Fig. 4]. As the N_2 gas flow increases, the energy of the nitrogen plasma increases and the grain size becomes bigger. The aggregation of the grains, the growth of the grain, can be promoted by the energy delivered by the plasma species.

The sheet resistance of plasma treated ITO films is presented as shown in Fig. 5. The resistance increases after N plasma treatment up to 20 sccm of N_2 flow, as expected [10, 11]. However, the reduction of resistance was found at a higher N_2 flow, 40 and 60 sccm, which has the plasma of increased 2nd positive series and decreased 1st negative series. In this region, a higher defect population was revealed from the UV-VIS results. It is

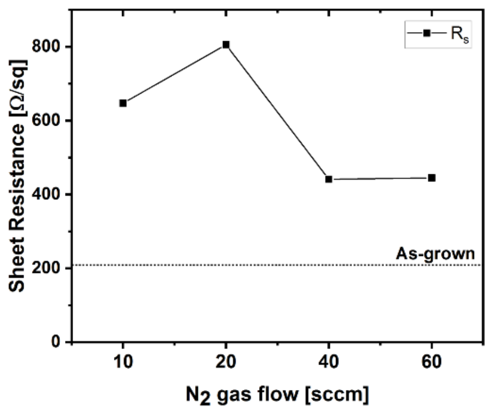

Fig. 5. Sheet resistance of as-grown and N plasma treated ITO films with a different N_2 flow.

difficult to identify the origin of the contradictory trend in the sheet resistance at this point without an assumption. More or less we can conclude that the increased energy of the excited neutral plasma species may lead to N doping, replace of O by N, as well as O vacancy defect generations, although the further studies are necessary in the future.

IV. CONCLUSION

We have studied the effects of nitrogen plasma treatment on ITO thin films. The energy and population of the nitrogen plasma of 1st, 2nd positive series (neutral molecules) and 1st negative series (ionic molecules) was altered by adjusting N_2 flow. Based on the comparative OSE study, we found that the energy of the excited neutral molecules is blue shifted with a higher N_2 flow, which was also revealed in aggregation of grains. In addition, the higher energy of exited neutral molecular nitrogen plasma leads to the decrease of the transmittance/ increase of the band tails and the reduction of the sheet resistance possibly due to the co-generations of the N dopings and O vacancies.

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