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## Oxygen annealing for deuterium doped indium tin oxide thin films

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### ABSTRACT

Deuterium doped indium tin oxide films, fabricated by *dc* plasma deposition in sputter gas consisting of deuterium and argon, were annealed at 300 °C for 40 min in flowing oxygen gas by using tubular gold image furnace. By the oxygen annealing, the optical transparency of the film deposited at the gas pressure ratio of deuterium to argon of 3.6 % increased from  $\approx 30$  to  $\approx 60$  % at the wavelength of 600 nm, although that of the films deposited at the ratios of 1 and 1.5 % slightly decreased from 88 to 80 % and from 85 to 77 %, respectively. The resistivity of the films at room temperature, ranged from  $2 \times 10^{-4}$  to  $1.4 \times 10^{-3}$   $\Omega\text{cm}$  corresponding to the gas pressure ratio from 1 to 3.6 %, was almost the same before and after the annealing for each film. Change in morphology toward smoother surface by the oxygen annealing was apparent especially for the film with the gas pressure ratio of 3.6 %. Agglomeration of randomly oriented grains with diameter of  $<100\sim 200$  nm observed before the annealing disappeared by the annealing. Smoother surface is responsible for higher transparency of the annealed films which contained densely populated hydroxyl bond before the annealing.

**KEYWORDS:** Oxygen annealing, Deuterium doped ITO, Optical transmittance, Hydroxyl bond

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## 1. INTRODUCTION

Indium tin oxide (ITO) has been used as transparent electrode material for optoelectronic devices by reason of its high optical transparency and low electrical resistivity. A great interest in low temperature deposition of ITO thin films is still now growing for fabrication of transparent electrodes compatible with organic material [1–5]. It is well known that the resistivity of ITO films deposited with soft sputtering parameters well-matched for organic substrate is rather high to be adopted as transparent electrodes. Films of ITO deposited by *rf* magnetron sputtering with argon containing oxygen of 0.2 % became highly conductive by annealing above 180 °C in a vacuum [5]. The electrical and optical properties of ITO films depend on local environments of chemical bonds. Oxygen vacancy has been believed to act as a double donor in  $\text{In}_2\text{O}_3$ . On the other hand, Lany and Zunger [6] proposed from their first principles calculation that oxygen vacancy results in persistent photoconductivity in  $\text{In}_2\text{O}_3$ . Dixit et al. [7] demonstrated that annealing at 600 °C in a high vacuum introduced excess carriers due to oxygen vacancy to  $\text{In}_2\text{O}_3$  thin film. The conductivity of the film changed from insulating to metallic by the vacuum annealing, although the optical transmittance stayed above 80 % even after the vacuum annealing. For poorly-crystallized ITO, oxygen vacancy is anticipated as a primarily source of *n*-type carriers, because Sn is not efficiently activated. In well-crystallized ITO, *n*-type carriers can be supplied from both oxygen vacancy and  $\text{Sn}^{4+}$  substituted for the  $\text{In}^{3+}$  site. Oxygen annealing is known to transform ITO films from opaque and resistive into transparent and conductive, respectively [8]. Crystallization temperatures between 150 and 200 °C were reported for transparent ITO films [9,10]. After annealing in air at 300 °C for 1 h, ITO films deposited on glass substrate by *rf* plasma sputtering exhibited the cubic *C*-rare earth type structure of  $\text{In}_2\text{O}_3$  [11]. Some heat treatments at 250–400 °C during or after deposition are known to be indispensable for activation of doped Sn. It is reported that diffusion of oxygen from an air atmosphere into ITO film can occur above 200~300 °C [2]. Below 300 °C, the optical transmittance of ITO films increased with a rise of the annealing temperature [12]. Heat treatments at 400 °C in a mixture of nitrogen and hydrogen gases and in an air dropped and recovered the transmittance of the ITO films, respectively [12]. Such behavior suggests that the loss and re-incorporation of oxygen are especially responsible for the optical property of ITO films.

Hydrogen has been anticipated to be beneficial to obtain highly conductive as-deposited ITO films without intentional substrate heating [13], although Shigesato and Yasui [14] showed that the resistivity of the ITO films deposited at 180 °C increased with an increase of

H<sub>2</sub>O partial pressure during deposition, and this was caused by decreases in both carrier density and Hall mobility. Recently, King et al. [15] suggested that hydrogen behaves as a shallow donor in In<sub>2</sub>O<sub>3</sub>. Furthermore, Limpijumnong et al. [16] clarified that hydrogen stayed at interstitial sites in In<sub>2</sub>O<sub>3</sub> lattice becomes shallow donors. In addition, Koida et al. [17] prepared hydrogen doped In<sub>2</sub>O<sub>3</sub> films on glass substrate by *rf* magnetron sputtering without substrate heating. For incorporation of hydrogen to the film, they introduced H<sub>2</sub>O vapor into a chamber during the deposition. They clarified that carriers of the as-deposited films are originated from doubly charged impurities, but those of the films annealed at 200 °C for 2 h in vacuum are due to singly charged impurities. We fabricated deuterium doped ITO thin films without intentional substrate heating by *dc* plasma deposition in sputter gas consisting of deuterium and argon [18–21]. The gas pressure ratios of deuterium to argon of the sputter gas from 1 to 1.5 % developed significant electrical conductivity ( $\approx 0.5 \times 10^4$  /Ωcm) while remaining the films optically transparent. However, the sputter gas with the ratio of 3.6 % gave rise to lowering in both the conductivity ( $\approx 1 \times 10^3$  /Ωcm) and the transparency (gray ITO). Rutherford backscattering spectroscopy for the films revealed that the richest oxygen vacancy corresponds to the lowest resistivity of the film which is fabricated in the sputter gas with the ratio of 1 %. X-ray photoelectron spectroscopy for the films demonstrated that the sputter gas with the ratio of 3.6 % gives rise to the richest hydroxyl bonded oxygen in the film. Deuterium in the sputter gas was incorporated into solid films, and stayed at interstitial sites of the lattice by forming hydroxyl bond.

Some improvements in performance as transparent electrodes by heat treatment after deposition are essential for hydrogen doped ITO thin films without intentional substrate heating. Nishimura et al. [22] fabricated ITO thin films by *dc* magnetron sputtering at room temperature (RT) using argon gas containing 1 % H<sub>2</sub>O, and then annealed the films from 120 to 350 °C for 1 h in nitrogen atmosphere. They clarified that crystallization is accomplished above 220 °C, and hydroxyl bonded species desorbs from the film above 250 °C. So, we attempted to examine the role of hydrogen, staying in the deuterium doped ITO films by forming hydroxyl bond, in the optical and electric performance by oxygen annealing at 300 °C. The oxygen annealing brought about a noticeable change in appearance of only the gray ITO film. The film deposited by the sputter gas with the ratio of 3.6 % became transparent optically, while appearance of the other films deposited by the sputter gas with the ratio of 1 and 1.5 % did not change by the annealing. The electrical properties remained at almost the same even after the annealing in spite of significant variation in population of the hydroxyl

bond.

## 2. PREPARATION of DEUTERIUM DOPED ITO THIN FILMS

Deuterium doped ITO thin films with thickness of  $\approx 200$  nm were deposited on glass substrate in the sputter gas containing deuterium by *dc* plasma sputtering without any heat treatments. We used a sintered target (Kojundo Chemical, Japan) with the composition of 95 wt. %  $\text{In}_2\text{O}_3$  and 5 wt. %  $\text{SnO}_2$ . The excitation conditions of columnar plasma for sputter deposition were as follows: gas pressure of  $\approx 1 \times 10^{-3}$  Torr, anode voltage of 75 V, and an anode current of 0.8 A. Deuterium gas (99.99 % purity) and argon gas (99.9999 % purity) were introduced to deposition chamber of the base pressure  $\approx 1 \times 10^{-7}$  Torr. Thin films were deposited at the deuterium gas partial pressures of  $\approx 1 \times 10^{-5}$ ,  $\approx 1.5 \times 10^{-5}$ , and  $3.6 \times 10^{-5}$  Torr. The gas pressure ratios of deuterium to argon [ $\text{D}_2$ ] were 1, 1.5, and 3.6 %. Deposition rate of the film amounted to  $\approx 0.6$  nm/min.

Deuterium incorporated in the as-deposited films was quantified by Rutherford backscattering spectroscopy-elastic recoil detection analysis method using the Tandem Accelerator installed at UTTAC in University of Tsukuba, Japan. Ions of  $\text{He}^+$  accelerated up to 2.5 MeV were injected at the angle of  $15^\circ$  to the sample surface. The recoiled ions and the back-scattered ions were collected by the detectors set at the angles of  $30^\circ$  and  $150^\circ$  with respect to the beam direction, respectively. The concentration of deuterium in the film [D] is shown in Fig. 1 (closed circle on the right hand scale). Almost linear increase of [D] with [ $\text{D}_2$ ] suggests that deuterium in the sputter gas reached the substrate surface and incorporated in the film almost quantitatively. The [D] value of the films deposited with [ $\text{D}_2$ ] of 1, 1.5, and 3.6 % were 0.16, 0.19, and 0.27 at. %, respectively.

X-ray photoelectron spectroscopy for the as-deposited films was carried out using a ULVAC-PHI model-1800L with monochromatized Al  $K\alpha$  radiation in vacuum pressure less than  $4.9 \times 10^{-9}$  Torr at RT. The O 1s higher binding energy side peak due to hydroxyl bonded oxygen ascended, but the O 1s lower binding energy side peak due to lattice oxygen descended with increasing the [ $\text{D}_2$ ] value, as shown in Fig. 1 (open circle on the left hand

scale). Deuterium located at the interstitial site of the  $\text{In}_2\text{O}_3$  lattice (the inset of Fig. 1) and formed hydroxyl bond in the film [21].

### 3. OXYGEN ANNEALING

The deuterium doped ITO films were heated at 300 °C for 40 min in flowing oxygen gas by using tubular gold image furnace.

Optical transmission spectra in the ultraviolet-visible wavelength region, measured by using a JASCO V-550 spectrometer, of the films before (closed circle) and after (open circle) the annealing are shown in Fig. 2. The optical transparency at the wavelength of 600 nm of the films deposited in the sputter gas with  $[\text{D}_2] = 1$  and 1.5 % decreased by 10 %, while that of the film with  $[\text{D}_2] = 3.6$  % increased from  $\approx 30$  to  $\approx 60$  % by the oxygen annealing. The gray film varied to transparent by the oxygen annealing.

Fig. 3 shows the resistivity (lower panel), carrier density (middle panel), and Hall mobility (upper panel) at RT of the films before (closed circle) and after (open circle) the annealing. The resistivity of the films, ranged from  $2 \times 10^{-4}$  to  $1.4 \times 10^{-3} \Omega\text{cm}$ , was changed hardly by the oxygen annealing. The carrier density ranged from  $8 \times 10^{20}$  to  $4 \times 10^{20} / \text{cm}^3$ , which is larger than those reported for the undoped and  $\text{H}_2\text{O}$  doped  $\text{In}_2\text{O}_3$  [7,17] and that of  $\text{H}_2\text{O}$  doped ITO [22] films. The Hall mobility ranged from 46 to 10  $\text{cm}^2 / \text{Vs}$  is almost the same to and rather small than those reported for the undoped and  $\text{H}_2\text{O}$  doped  $\text{In}_2\text{O}_3$  [7,17] and that of  $\text{H}_2\text{O}$  doped ITO [22] films. Electron transport of the deuterium doped ITO films was scarcely affected by the oxygen annealing.

X-ray diffraction pattern of the films before and after the annealing measured with a Rigaku CN2013 diffractometer using  $\text{Cu } K\alpha$  radiation are shown in Fig. 4. Both panels show polycrystalline structure of the films with the *C*-rare earth type  $\text{In}_2\text{O}_3$ . The main growth planes were (222), (400), (440), and (622) for the film before the annealing. After the annealing, the (420) plane appeared additionally to those of before the annealing. Re-crystallization and re-growth of the  $\text{In}_2\text{O}_3$  lattice were prompted by thermal energy of 300 °C. For *dc* magnetron sputtered ITO film, annealing in oxygen at 100 °C after the deposition gave rise to the

resistivity of  $7 \times 10^{-4} \Omega\text{cm}$  and re-growth of grains with the preferential (222) orientation [23]. Re-crystallization, coalescence, and agglomeration of grains by annealing at 250 °C for 30 min in a He atmosphere were reported for polycrystalline ITO thin films deposited by *rf* magnetron sputtering at RT [24]. However, crystallization cannot explain the change in the optical property because the change in x-ray diffraction pattern was common for all the films. Therefore, the optical and electrical properties may depend on the availability of oxygen during the thermal transformation.

The O 1s photoelectron spectra shown in Fig. 5 indicate that population of the hydroxyl bonded oxygen was reduced by the oxygen annealing. After the annealing, the intensity ratio of hydroxyl bonded oxygen to lattice oxygen decreased to  $\approx 1$  for all the films in spite of a large difference in the ratio among the films before the annealing. The reduction is especially significant for the film deposited in the sputter gas with  $[\text{D}_2] = 3.6 \%$ . The oxygen annealing caused dissipation of the hydroxyl bonded oxygen. Such a change in the dominant species to lattice oxygen matches up to an increase of the optical transmittance for the film deposited in the sputter gas with  $[\text{D}_2] = 3.6 \%$ . Oxygen diffusion between the film and ambient atmosphere can occur at 300 °C [2,11]. Even below 300 °C, optical transparency has been reported to increase by annealing [12]. Savu and Joanni [25] reported that surface appearance of the films was strongly influenced by the decrease of oxygen concentration in the ambient gas.

Surface morphology before and after the annealing of the films was examined by a JEOL JSM-6360 scanning electron microscope operated at the electron acceleration voltage of 15 kV. As shown in Fig. 6, change in morphology of the film with  $[\text{D}_2] = 1 \%$  was not apparent; the surface was the smoothest before and after the annealing. We see disappearance of sparsely distributed grains with diameter of  $<100\sim 200$  nm on the film with  $[\text{D}_2] = 1.5 \%$ . The change in morphology toward smoother surface by the annealing was obvious for the film with  $[\text{D}_2] = 3.6 \%$ . Randomly oriented grains with diameter of  $<100\sim 200$  nm agglomerated at the surface before the annealing. The agglomeration disappeared pronouncedly by the oxygen annealing at 300 °C. The annealing at 400 °C for the ITO films *rf* sputter deposited on glass substrate at RT was reported to lead to better conductivity and transparency due to larger

grain size with the lowest scattering coefficient [26]. Smoother surface morphology lowers scattering coefficient and enhances optical transmittance of the annealed films.

#### 4. CONCLUSION

Oxygen annealing at 300 °C distinguished the role of hydroxyl bonded species playing in the optical and electric performance of the deuterium doped ITO thin films. Hydrogen in the atmosphere during plasma sputtering deposition has a significant influence on lattice defects of ITO films, such as oxygen vacancy and hydrogen stayed at the interstitial site by forming hydroxyl bond. The oxygen annealing caused a noticeable change in appearance of the gray ITO film. The film deposited in the sputter gas of  $[D_2] = 3.6\%$  looked grayish before the annealing became transparent after the annealing. The oxygen annealing at 300 °C decreased population of deuterium stayed at the interstitial site, and smoothed the film surface. Disappearance of agglomerated grains with diameter of  $<100\sim 200$  nm is responsible for higher transparency for the film after the oxygen annealing. Despite a prominent change in transparency of the gray ITO film, electrical properties were scarcely affected by the oxygen annealing. Even for the gray ITO film, the transport properties remained at almost the same before and after the annealing. Deuterium stayed at the interstitial site deteriorated the optical transparency by forming hydroxyl bonded species such as In-OD, but scarcely affected the electric property since the deuterium related species can play the role of singly charged impurity in ITO. Therefore, oxygen vacancy dominated the electrical property and deuterium at the interstitial site influenced on the optical property of the as-deposited deuterium doped ITO thin films.

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## FIGURE CAPTIONS

Figure 1 Atomic concentration of deuterium (closed circle on the right scale) and O 1s peak intensity ratio of hydroxyl bonded oxygen to lattice oxygen (open circle on the left scale) of the as-deposited films. Inset: schematic illustration of deuterium located at the interstitial site of the  $\text{In}_2\text{O}_3$  lattice.

Figure 2 Optical transmittance spectra of the films deposited with  $[\text{D}_2]$  of 1 % (a), 1.5 % (b), and 3.6 % (c) before (closed circle) and after (open circle) the annealing.

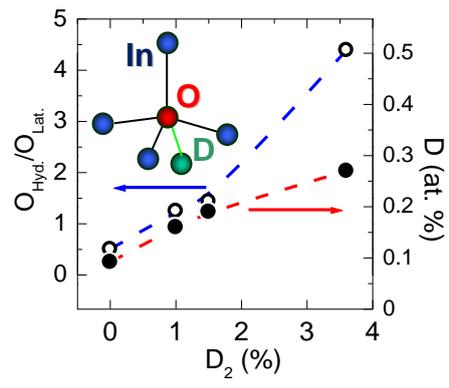
Figure 3 Electrical resistivity  $\rho$  (lower panel), carrier density  $N$  (upper panel), and Hall mobility  $\mu$  (upper panel) of the films before (closed circle) and after (open circle) the annealing.

Figure 4 X-ray diffraction pattern of the films deposited with  $[\text{D}_2]$  of 1 % (a), 1.5 % (b), and 3.6 % (c) before (lower panel) and after (upper panel) the annealing. The arrows in the upper panel indicate crystalline peaks due to solder used for electrical measurements.

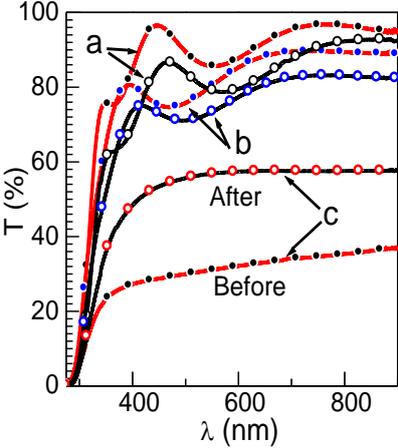
Figure 5 O 1s photoelectron spectra of the films deposited with  $[\text{D}_2]$  of 1 % (a), 1.5 % (b), and 3.6 % (c) before (closed circle) and after (open circle) the annealing. The arrows at  $\approx 530$  eV ( $\text{O}_{\text{Lat.}}$ ) and  $\approx 532$  eV ( $\text{O}_{\text{Hyd.}}$ ) indicate the peak originated from lattice oxygen and hydroxyl bonded oxygen, respectively.

Figure 6 Surface morphology of the films deposited with  $[\text{D}_2]$  of 1 % (a), 1.5 % (b), and 3.6 % (c) before (left row) and after (right row) the annealing.

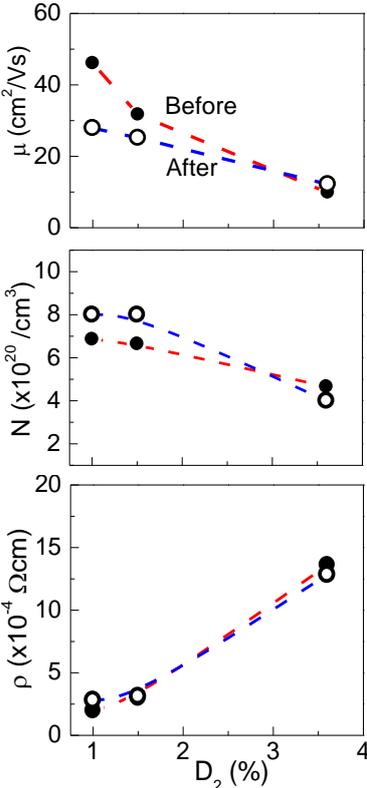
K.O Fig. 1



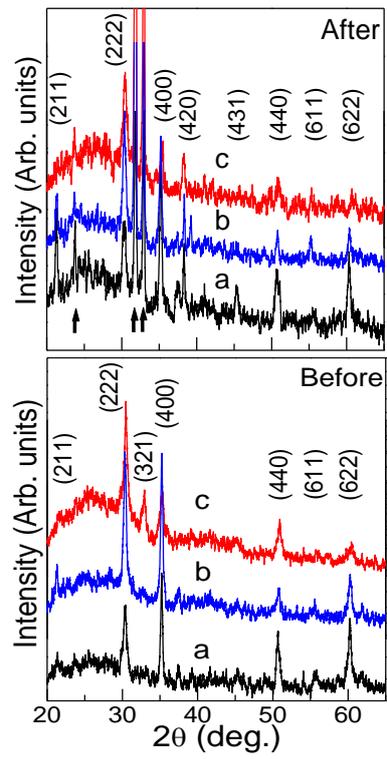
K.O Fig.2



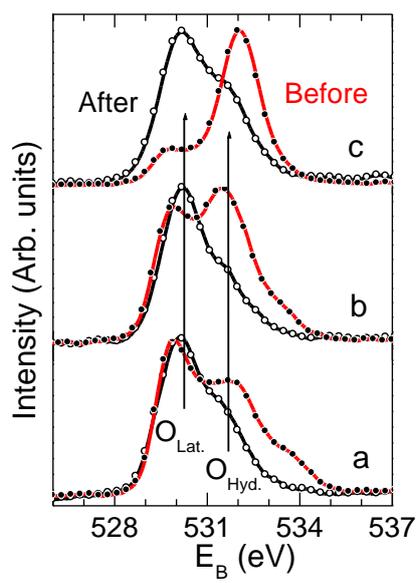
K.O Fig. 3



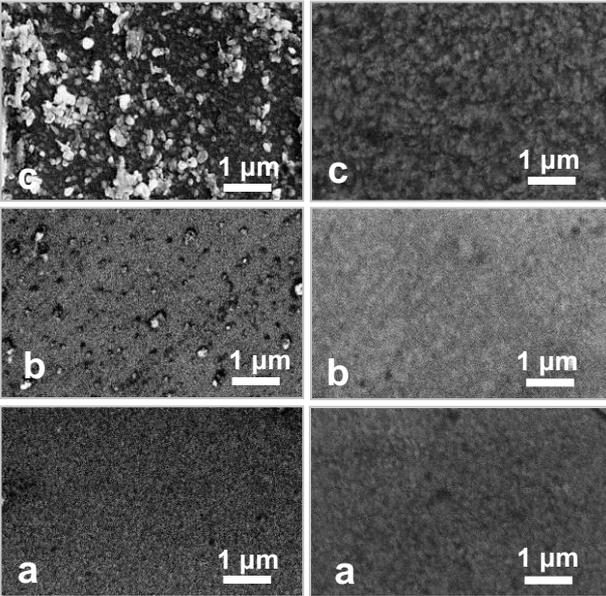
K.O Fig. 4



K.O Fig. 5



K.O Fig. 6



TOC figure by K.O

