Special Feature: Applied Nanoscale Morphology

Degradation Mechanism of Organic Light Emitting Devices Originating from Transparent Electrodes

Toshikazu Satoh, Hisayoshi Fujikawa, Takanori Murasaki, Ichiro Yamamoto, Yoshifumi Kato and Yasunori Taga

■**ABSTRACT**‖ A thin organic layer on indium tin oxide (ITO) was analyzed by X-ray photoelectron spectroscopy (XPS) to examine the poor characteristics of the organic light emitting diode (OLED) that uses an ITO anode deposited at room temperature (ITO-RT) and the degradation of OLEDs by photo-irradiation. A large number of the hydroxyl groups that originate in the amorphous structure of the ITO-RT electrode were identified. The hydroxyl groups of ITO-RT are presumed to oxidize the organic layer deposited on ITO-RT. The oxidation loses the characteristics of the OLED by decreasing the conductivity of the organic layer. Photo-irradiation makes peak shifts of the organic component in the XP spectra. The peak shifts suggest the change of the electronic structure, which leads to the increase of the hole injection barrier height at the ITO/organic interface. Growth of the organic oxide layer by photo-irradiation was also identified. The organic oxide layer accelerates the degradation of OLEDs, because it generates a high resistance layer and affects the electronic structure at the interface. Degradation of OLEDs by photo-irradiation is therefore attributable to the ITO electrodes, because oxygen atoms are supplied from the ITO electrodes.

■**KEYWORDS**‖ Indium Tin Oxide, Organic Light Emitting Diode, Interface, X-ray Photoelectron Spectroscopy, Oxidation

1. Introduction

Organic light emitting diodes (OLEDs) have drawn attention as flat panel displays and light sources. Because of their attractive potential for such applications, numerous efforts to improve the performance of OLEDs have been made since the first report by Tang and VanSlyke.[1] Since luminous decay has been a serious problem for the practical use of OLEDs, analyzing the degradation mechanism and improving the lifetime have been a major part of the research reports of OLEDs.[2-8]

OLEDs commonly consist of several organic layers and inorganic electrodes. Because of the necessity of extracting light emission, at least one electrode is required to be transparent in the visible range. Indium tin oxide (ITO) is the most widely used material for the transparent electrode in an OLED. ITO has the following attractive properties as the anode material in an OLED: high transparency in the visible range, low electric resistivity, high work function, and relative ease in the patterning process.[9-12] The properties of ITO electrodes have been reported to affect the characteristics of OLEDs. For example,

surface treatments of ITO electrodes, such as UV-ozone treatment,[12] oxygen plasma bombardment,[13] and self-assembled monolayer modification,[14,15] have been reported to alter the work function of ITO electrodes, which alters the driving voltage and luminous efficiency.

The properties of ITO electrodes also affect the degradation behavior of OLEDs. Although ITO electrodes are commonly deposited on heated glass substrates, ITO electrodes must be deposited without heated substrates in the case of substrates having poor heat resistance. Our previous research revealed that an OLED constructed on an ITO electrode deposited at room temperature (ITO-RT) exhibits a higher driving voltage and a shorter lifetime than that on the ITO electrode deposited by heating the substrate (ITO-HT).[16] Heil et al. reported that the photo-degradation of polymer OLEDs occurred by irradiation of the visible and near-ultraviolet light and the degradation was the result of a chemical reaction occurring at the interface between the organic layer and the ITO electrode.[17] In other words, such poor characteristics result from chemical and electronic interaction at the interface between ITO electrodes

and organic layers. However, these interfacial interactions have not been thoroughly examined.

X-ray photoelectron spectroscopy (XPS) is one of the most effective methods to analyze the chemical interaction and the profiles affected by electronic transformation. Therefore, we made an attempt to examine the interaction between ITO electrodes and organic layers by analyzing a thin organic layer on an ITO film by using XPS. In this article, we report the effects of substrate temperature in the deposition process of ITO electrodes and the effects of photo-irradiation on the interaction between ITO electrodes and organic layers.

2. Experimental Procedure

Substrates of 100-nm thick ITO films were deposited on thermally oxidized silicon (001) and on glass substrates by RF-magnetron sputtering in an ambient Ar/O_2 mixture by using a sintered ceramic target of 10-wt% SnO_2-doped In_2O_3. The ITO films deposited on the glass or oxidized silicon substrates with and without external heat (573 K with heat) are defined as ITO-HT and ITO-RT, respectively, in this article. The conditions for the sputter deposition and the properties of the ITO films are shown in **Table 1**. The resistivity was calculated from the sheet resistance, which was measured by the four-point probe method, and the ionization potential was determined by photoemission.[18] X-ray diffraction (XRD) of the ITO films on glass in θ-2θ geometry was carried out to analyze the crystallographic structure.

The ITO-coated substrates were cleaned by ultrasonic cleaning in organic solvents and UV-ozone treatment. Then, the substrates were introduced into the analysis equipment schematically shown in **Fig. 1**. The substrates were transferred into the analysis chamber and analyzed by XPS with Mg-Kα irradiation. The substrates were subsequently transferred into the evaporation chamber, and 3-nm thick triphenyltetraamin (TPTE) layers were evaporated onto them.[19,20] After the evaporation, the substrates were transferred into the analysis chamber again and analyzed by XPS. Photo-irradiation of the TPTE-evaporated sample using ITO-HT was carried out up to 80 h to examine the photo degradation. The irradiation source included 12 commercially available violet light emitting diodes (7.7 mW), which were placed against a viewing port made of fused silica. The distance between the light source and the sample was about 150 mm. Evaporation, photo-irradiation and XPS analysis were subsequently carried out without breaking the vacuum. The binding energy in each XP spectrum was calibrated by that of the In_2O_3 component (443.7 eV) in In $3d_{5/2}$ core level spectra in this work.[21]

3. Results and Discussion

3. 1 Origin of the Poor Characteristics of the OLEDs Using ITO-RT

Figure 2 shows the XRD profiles of the ITO films on glass substrates. The profiles indicate that the crystallographic structure of ITO-RT was amorphous, and that of ITO-HT was a polycrystalline In_2O_3-type structure with (111) preferred orientation. **Figure 3** shows the O 1s core level XP spectra of the ITO substrates. The feature of the spectra that is different is the substrate temperature in the deposition process of ITO. However, peak fitting of the spectra using the Voigt function revealed that each substrate has two

Table 1 Conditions for sputter deposition and electrical properties of ITO electrodes.

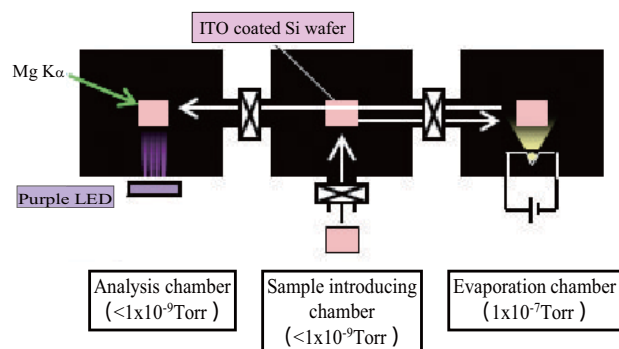|	ITO-RT	ITO-HT
Substrate Temperature	RT	573 K
Processing gas	Ar – 2 vol% O_2	Ar – 1 vol% O_2
Pressure	2×10^{-3} Torr	3×10^{-3} Torr
Input rf-Power	200 W	200 W
Deposition Rate	6.7 nm/min	6.7 nm/min
Resistivity	5.1×10^{-4} Ω·cm	1.6×10^{-4} Ω·cm
Ionization Potential	5.48 eV	

Fig. 1 Schematic of analysis equipment.

chemical states of oxygen: one state is the bonds with indium as oxygen atoms (530.3 eV, In-O-In) and the other state is the bonds with indium as hydroxyl groups (531.5 eV, In-OH).[21] The difference of the feature of the spectra originates from the ratio of the two states, since the relative ratio of hydroxyl groups in the whole spectrum is much higher in ITO-RT. Because the crystallographic structure of ITO-RT was amorphous, as mentioned above, ITO-RT is considered to have more defects than ITO-HT. Since crystallographic defects are a favorable adsorption site of H_2O molecules,[22] many hydroxyl groups could adsorb on the defects of ITO-RT by the air exposure. The difference in the crystallographic structure therefore generates the difference in chemical states between ITO-RT and ITO-HT.

Figure 4 shows the O 1s core level XP spectra of the 3-nm thick TPTE layers deposited on the ITO-RT and ITO-HT substrates. Although there are no oxygen atoms in a TPTE molecule, the feature of the spectra is different from that of the ITO substrates, especially in the TPTE layer on ITO-RT. Peak fitting of the spectra revealed that transformation of the O 1s spectra is due to the generation of the chemical bonding between carbon and oxygen, such as C-O-C (533.3 eV) and C=O (532.2 eV), as indicated in the spectra.[23] It is therefore considered that TPTE molecules deposited onto ITO substrates are oxidized by the oxygen atoms existing at the surface of the substrates. The contributions of C-O-C and C=O bonds in the spectrum of TPTE on ITO-RT are observed, while only a scarce contribution of the C-O-C bond is identified in the spectrum of TPTE on ITO-HT. In addition, the contribution of the In-OH bond in the spectra of ITO-RT exhibits a large decrease by the deposition of TPTE. These results suggest that the oxidation of the TPTE molecules originates from the hydroxyl groups at the surface of ITO. Since ITO-RT has many more hydroxyl groups than does ITO-HT, as described above, oxidation of TPTE molecules would be promoted much more on ITO-RT than on ITO-HT.

As previously mentioned, the OLED constructed on an ITO-RT anode exhibits higher driving voltage and a shorter lifetime than that on an ITO-HT anode. The results in this work indicate that there is a difference in the chemical interaction at the TPTE/ITO interface; the magnitude of the oxidation of hole transporting material (HTM) such as the TPTE face on an anode is much larger in the case that ITO-RT is an anode. Although there has been little knowledge of the effects of the oxidation of HTM on the characteristics of OLEDs, Kieffel et al. reported that polyaniline, which is widely known as an organic conducting material, decreases its conductivity by about two orders due
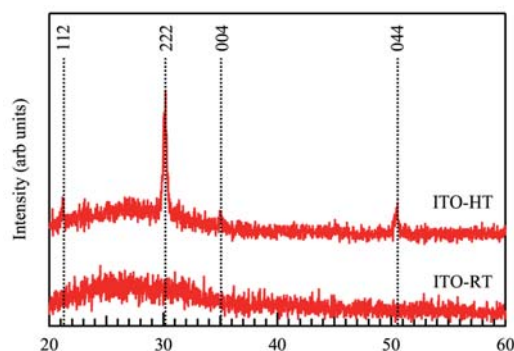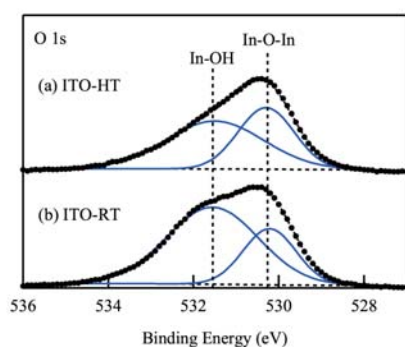

Fig. 2   XRD profiles of the ITO films.

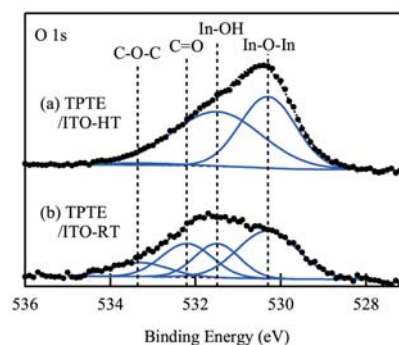**Fig. 3**   O 1s XPS spectra of (a) ITO-HT, and (b) ITO-RT.

Fig. 4   O 1s XPS spectra of 3-nm thick TPTE deposited on (a) ITO-HT, and (b) ITO-RT.

to the oxidation.[24] It is therefore expected that the oxidation of HTM would decrease its conductivity, which would affect the driving voltage of OLEDs. The increase of the driving voltage means the increase of the Joule heat in OLEDs. Because the degradation of an organic semiconductor is accelerated by the increase of temperature in general, the increase of the Joule heat in OLEDs would accelerate their degradation. Therefore, the oxidation of HTM would decrease the lifetime of OLEDs.

The above results suggest that oxidation of an HTM layer caused by a large quantity of hydroxyl groups originating from the amorphous structure leads to the high driving voltage and short lifetime of the OLED using an ITO-RT anode.

3. 2 Mechanism of the Photo Degradation of OLEDs

Figure 5 shows the C 1s core level XP spectra of the TPTE film on the ITO-HT film before and after photo-irradiation. Peak fitting revealed that each spectrum was made up of two components, indicated as C1 and C2. Given the molecular structure of TPTE, the components C1 and C2 correspond to aromatic carbon of the benzene rings and carbon linked to nitrogen, respectively.[25] Although the

photo-irradiation did not alter the difference of the peak binding energy and the integral intensity ratio between C1 and C2, it displaced each peak position toward the higher binding energy side. The degree of the peak shift after the 20-hour irradiation was 0.3 eV, and only a minimal additional peak shift was observed by further irradiation. Such a peak shift by photo-irradiation without changing its shape was also observed in the N 1s spectrum. The peak shift was almost completed by the 20-h irradiation as was the C 1s spectrum, and its magnitude was 0.2 eV.

The O 1s core level XP spectra of the 3-nm thick TPTE on ITO-HT before and after photo-irradiation are shown in **Fig. 6**. Each spectrum was fitted by using three components of the Voigt function: O1, O2 and a slight contribution of O3. As previously described, O1, O2, and O3 correspond to the In-O-In bonds, In-OH bonds, and organic oxygen, respectively. Although a slight peak binding energy shift was observed in O1 and O2, the peak binding energy of O3 was shifted toward the higher binding energy side along with C 1s and N 1s. The peak binding energy shift of O3 was also almost completed after the 20-h photo-irradiation, and the magnitude of the shift was 0.2 eV. On the other hand, the O3 contribution in the whole O 1s spectra increased with the irradiation time from the initial stage of irradiation to the end of the
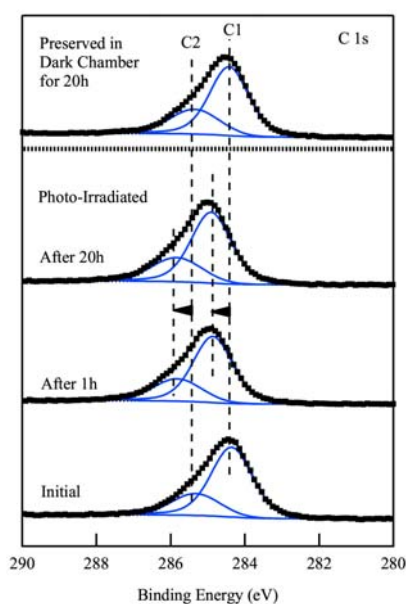

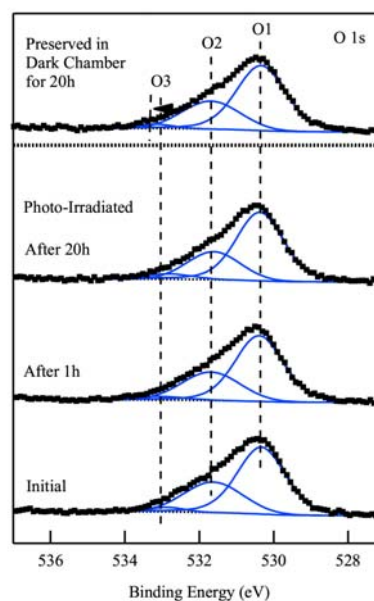**Fig. 5**   C 1s XPS profiles after photo-irradiation.

Fig. 6   O 1s XPS profiles after photo-irradiation.

experiment.

Photo-irradiation caused the following two changes. The first is a peak shift of C 1s, N 1s and the organic component of the O 1s spectra observed in the initial stage of irradiation, and the second is an increase in the area ratio of the organic component in the O 1s spectrum.

First, the peak shift is discussed in this section. Since all the components for the observed peak shifts originated from the organic molecule, photo-irradiation affected the chemical state of TPTE or the electronic structure at the interface between TPTE and ITO. In general, a change in the chemical states accompanies the alternation of the peak shape and the peak shifts in different directions in the XP spectra. The peak shape of C 1s, however, showed little change and each peak shift showed the same direction and similar time dependence. The change of the chemical state of TPTE is therefore hardly considered. Then, the change in the electronic structure is examined. An abrupt vacuum level shift relative to the Fermi level at the electrode/organic interface has been reported.[26] The vacuum level shift at the interface shifts the XPS peak originating from the organic layer in the same direction relative to the peak originating from the electrode without changing its shape, if the binding energy of the spectra is corrected by the peak binding energy of the element in the electrode. The peak shifts of the organic elements to a higher binding energy originate from the change of the electronic structure at the interface, because the peak shifts observed in this work can be explained by this model. The peak shifts suggest that the HOMO level of TPTE shifts to a relatively deeper level from the Fermi level of ITO. The foregoing relative HOMO level shift means an increase in the hole injection barrier height at the TPTE/ITO interface.

Next, the increase in the area ratio of the organic component in the O 1s spectrum is discussed. The continuous increase of the organic component of oxygen in the spectrum by photo-irradiation suggests the progression of the oxidation of TPTE. **Figure 7** shows the emission spectrum of the violet LED used in this work and the absorption coefficients of TPTE and ITO. The peak wavelength of the violet LED was 380 nm, and the emission range was between 370 nm and 420 nm. The absorption edge of ITO was about 350 nm, and ITO showed little absorbance at the wavelength of the LED. Since the absorption edge of

TPTE was 420 nm, which is a longer wavelength than the whole emission of the LED, the band gap of TPTE is smaller than the energy of the light source. Since the band gap of TPTE is smaller than the energy of the LED, TPTE molecules are expected to be excited by the photo-irradiation. In addition, triphenyldiamine (TPD), which is composed of the same functional groups as TPTE, is reported to generate TPD cations under UV-irradiation when TPD is mixed with oxidizing inorganic salts or compounds,[27] and the ability to generate TPTE cations by photo-irradiation in this experiment is therefore expected. On the other hand, there are hydroxyl groups, adsorbed water molecules, and intra-crystalline oxygen atoms at the surface and inside the ITO films. TPTE molecules in the activated state, as described above, would react with these oxidation sources and generate oxidized TPTE molecules. As described above, OLEDs, which have an oxidized TPTE layer at the organic/ITO interface, exhibit a high driving voltage. Therefore, progressing of oxidation of TPTE by photo-irradiation also affects the characteristics of OLEDs.

The above results indicate that degradation of OLEDs could take place even in OLEDs using an ITO-HT anode. The degradation is caused by the increase of the hole injection barrier and the generation of the high resistance layer, both of which lead to the degradation of the organic layer by the increase of the driving voltage of OLEDs. The dipole of the organic oxide layer affects the electronic structure at the interface. Therefore, the increase of the hole injection barrier is considered to be due to the oxidation. As described above, the generation of the high resistance layer is also caused by the oxidation of the organic
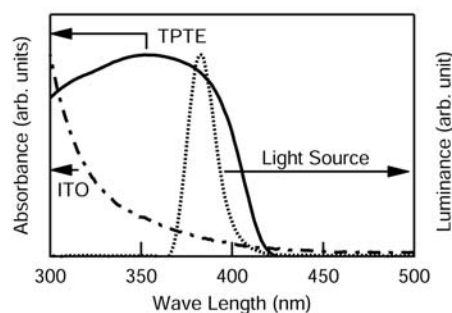

Fig. 7   The emission spectrum of the light source and light absorbance spectra of TPTE and ITO.

molecules. The degradation of OLEDs by the photo-irradiation is therefore caused by the oxidation of the organic molecules at the organic/ITO interface. This work revealed that the degradation of OLEDs by photo-irradiation is attributable to the ITO electrodes, because the oxygen atoms are supplied from the ITO electrodes.

4. Summary

A thin TPTE layer on ITO was analyzed by XPS to examine the poor characteristics of the OLEDs using ITO-RT and the photo degradation of the OLEDs using ITO-HT, and the following results were obtained.

(1) ITO-RT has an amorphous structure and a larger quantity of hydroxyl groups than does ITO-HT. A large quantity of hydroxyl groups easily oxidizes the TPTE layer. It is suggested that the oxidation of the TPTE layer results in the high driving voltage and the short lifetime of OLEDs using ITO-RT anodes by decreasing their conductivity.

(2) Peak shifts toward the higher binding energy of the components originating from organic molecules (C 1s, N 1s, and the organic component in O 1s) were observed by photo-irradiation. The progression of oxidation of the TPTE layer was observed at the same time. These results suggest the increase of the hole injection barrier from the ITO anode, and the growth of the low conductance layer at the interface.

The above results indicate that the poor characteristics of the OLEDs using ITO-RT and the photo degradation of the OLEDs using ITO-HT are both associated with the oxygen atoms and the hydroxyl groups in ITO. Since ITO is an oxide material, oxidation of the organic layer should be considered in the design of OLEDs.

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Table 1 and Figs. 3-4
Reprinted from Appl. Phys. Lett., Vol. 87, No. 14 (2005), 143503, Satoh, T., Fujikawa, H. and Taga, Y., Influence of Indium Tin Oxide Electrodes Deposited at Room Temperature on the Properties of Organic Light-emitting Devices, © 2005 AIP, with permission from American Institute of Physics.

Figs. 5-7
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