Electrical Engineering in Japan, Vol. 154, No. 4, 2006
Translated from Denki Gakkai Ronbunshi, Vol. 125-A, No. 4, April 2005, pp. 379–384

Effect of Oxygen Plasma Treatment of Indium Tin Oxide for Organic Solar Cell

YUICHI HASHIMOTO[1] and MANABU HAMAGAKI[2]
[1]Canon Inc., Japan
[2]RIKEN, Japan

SUMMARY

We have investigated the contribution of oxygen ions and electrons in the oxygen plasma treatment of an indium tin oxide (ITO) electrode for organic solar cell (ITO/CuPc/C_{60}/CuPc/Al). The cell characteristics were markedly improved by the treatments using positive oxygen ions and electrons. In the case of treatment by positive oxygen ions, short-circuit photocurrent density increased markedly. The enhancement of photocurrent was explained in terms of a lowering of the total resistance between the CuPc layer and ITO due to an increase in the work function and highly oriented stacking in CuPc molecular configurations during the growth process. In the case of treatment by electrons, on the other hand, the fill factor showed a high value of about 0.5. However, further studies are needed for confirmation of this phenomenon. © 2006 Wiley Periodicals, Inc. Electr Eng Jpn, 154(4): 1–7, 2006; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/eej.20313

Key words: oxygen plasma; organic solar cell; ITO; fullerene; copper phthalocyanine.

1. Introduction

Organic solar cells using organic dyes [1–5] have attracted much attention as promising low-cost photovoltaic devices, since an energy conversion efficiency of 7.9% in a solar cell based on a TiO_2-ruthenium complex was realized by O'Regan and Grätzel in 1991 [6]. Indium tin oxide (ITO) has been widely used as an electrode in organic functional devices because of its transparency, high conductivity, and capability of carrier injection into the organic layer. Recently, it has been shown that characteristics of organic light emitting diodes (OLED), such as efficiency and brightness, are significantly improved by plasma treatment of ITO [7–14]. The work function of ITO, in particular, is critical to device performance because it affects the hole injection ability at the interface between the ITO and the hole transport layer (HTL) in OLED. Oxygen plasma treatment of ITO is now widely used as one of the most effective ways to increase the work function of ITO and to improve the device performance of OLED [7–14]. The performance of organic functional devices is strongly influenced by the properties of the interfaces between the constituent organic layers and the electrodes. Since the organic dyes used in organic solar cells are similar to those of the OLED, the electronic properties of the electrode surface are expected to directly affect the cell characteristics, resulting in carrier transport between the constituent organic layers and the electrodes. The plasma sources described above were mainly generated by microwave and rf plasma; however, one inadequacy of these treatments was that the analysis was not sufficient to identify the separate contributions of oxygen ions and electrons.

In the present work, we have investigated the cell characteristics of ITO/copper phthalocyanine (CuPc)/C_{60}/CuPc/Al devices to determine the independent contribution of oxygen ions and electrons, and the treatment energy dependence of the oxygen plasma treatment of ITO using an electron-beam-excited plasma (EBEP) [15]. The experimental result showed that treatment by positive ions and electrons in oxygen plasma is an effective way to modify the electronic properties of the ITO surface, markedly improving the cell characteristics. Moreover, we have examined the influence of the molecular configurations and electronic properties of the CuPc layer on the photocurrent of the cell.

2. Experimental Procedure

The substrates used in the present experiments were ITO-coated glass (Nippon Sheet Glass Co., Ltd.). The ITO layer was deposited by reactive sputtering at low oxygen gas pressure. The thickness, resistivity, and active electrode area of the ITO layer were 110 nm, 12 Ω/□, and 3.14×10^{-2} cm^2, respectively. The grain size of 35 to 50 nm and the roughness (Rz: mean value of 30 data) of about 30 nm on the ITO surface were determined by atomic force microscopy (SPI-3800, SII Nano Technology Inc.) in 5 × 5-μm scans. The ITO-coated glass substrates were first ultrasonically cleaned for 30 min in acetone and then degreased for 30 min by isopropyl alcohol vapor. They were transferred immediately from the atmosphere to an oxygen plasma treatment and deposition chamber (Fig. 1), which was attached to an electron-beam-excited plasma (EBEP) system [15].

The EBEP system consists of three sections: (I) a plasma cathode region (not shown in figure), (II) an electron acceleration region (not shown in figure), and (III) an electron-beam-excited plasma region as described above. The base pressure of the chamber was 1.4×10^{-4} Pa. The oxygen gas was fed into the chamber and the gas pressure in the chamber was maintained at about 0.2 Pa using a mass flow controller. The electrons in the plasma cathode region (acceleration voltage of 60 V, discharge current of 1.5 A) were injected into the chamber along an axial magnetic field. An oxygen plasma density of about 10^{10} cm^{-3} was produced in the chamber by the electron beam.

We investigated the effects of the species, that is, oxygen ions and electrons, during oxygen plasma treatment on the electronic properties of the ITO and on the cell characteristics. For oxygen plasma treatment, the ITO substrates were exposed to different species of the oxygen plasma for 30 s with application of a DC voltage (V_t: treatment voltage) in the range from −70 to 40 V to the ITO layer. The ITO layer was treated with electrons in the case of positive treatment voltage, that is, electron treatment, and with positive oxygen ions in the case of negative treatment voltage, that is, oxygen ion treatment. In this system, the voltage (V_t) applied to the ITO layer during treatment corresponds to the incidence kinetic energy of the species, that is, oxygen ions and electrons. The values of current density incident on the ITO layer were about 20 mA/cm^2 in the case of the positive treatment voltage (electron treatment), and 1.5 mA/cm^2 or less in the case of the negative treatment voltage (oxygen ion treatment).

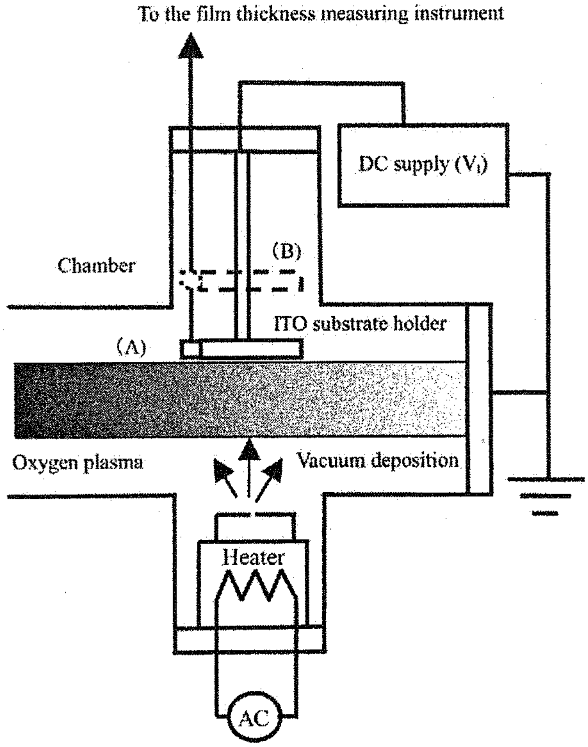


Fig. 1. Schematic diagram of the vacuum chamber with oxygen plasma treatment system.

After the above treatments, a copper phthalocyanine (CuPc, TriChemical Laboratories Inc.) layer was deposited on the ITO layer by conventional vacuum deposition at a base pressure of 1.4×10^{-4} Pa to obtain a thickness of 35 nm with a deposition rate of 0.1 nm/s. Fullerene (99.95% C_{60}, Materials and Electrochemical Research Corp., deposition rate of 0.05 nm/s), CuPc (TriChemical Laboratories Inc., deposition rate of 0.1 nm/s), and Al (deposition rate of 0.5 nm/s) were deposited on the CuPc layer with thicknesses of 13, 25, and 100 nm, respectively. After its deposition, the Al was encapsulated in a glass bottle containing calcium oxide powder and epoxy in a dry box.

The current–voltage characteristics under photo-irradiation (AM1.5, 100 mW/cm^2) were then measured using a 300-W xenon lamp and an electrometer (R6246, ADVANTEST) under atmospheric conditions at 22 °C. The ITO and Al electrodes acted as hole collecting and electron collecting electrodes, respectively.

The work function of the ITO after the oxygen plasma treatments was measured in air using a Kelvin probe (FAC-1, Riken Keiki Co., Ltd). The properties of the CuPc layer on the ITO surface treated by the oxygen plasma were investigated by various experimental techniques. The ionization potential and Fermi level of the CuPc and the current–voltage characteristics for a microscopic area of the ITO/CuPc interface were examined using a low-energy photoelectron counter (AC-1, Riken Keiki Co., Ltd) [16], a Kelvin probe (FAC-1, Riken Keiki Co., Ltd), and an atomic force microscope (AFM: SPI-3800, Seiko Instruments Inc.), respectively. The crystallinity of the CuPc layer was examined by X-ray diffraction (XRD: RINT2000, Rigaku Corp.) with a Cu-Kα X-ray source.

3. Results and Discussion

The low power conversion efficiency of organic solar cells is mainly related to their low carrier mobility, low absorption, and small exciton diffusion lengths, limiting the active area around the interfaces, such as electrode/organic layer and organic layer/organic layer, for exciton dissociation. The organic solar cell studied in this work used a three-layer structure, ITO/CuPc/C_{60}/CuPc/Al, following the idea that a combination of two different molecules is an effective way to enlarge the open voltage and photocurrent of the cell. The CuPc/C_{60}/CuPc structure of the cell uses two molecules with different transport properties, considering C_{60} as n-type and CuPc as p-type. In the as-grown ITO/CuPc (thickness of 20 to 60 nm)/Al devices, the short-circuit photocurrent density was several tens of μA/cm^2, in contrast to the open-circuit voltage of about 500 mV. In the as-grown ITO/CuPc (thickness of 20 to 60 nm)/C_{60} (thickness of 8 to 30 nm)/Al devices, on the other hand, the open-circuit voltage decreased to about 200 mV or less, in contrast to a hundredfold increase of short-circuit photocurrent density. These experimental results suggest the following: (i) the contact potential difference at the CuPc/Al interface plays an important role in the open-circuit voltage, (ii) the C_{60} layer, as a consequence of the long excitation diffusion length of 7.7 ± 1 nm [16], contributes to an increase of the short-circuit photocurrent density. In the ITO/CuPc/C_{60}/CuPc/Al device, since the CuPc/C_{60}/CuPc layer is considered to be a p-n-p structure, we assumed that the contact potential difference of the CuPc/C_{60}/CuPc layer is negligible.

Figure 2 shows the photocurrent–voltage characteristics of cells built on ITO substrates treated by oxygen plasma at an irradiation intensity of 100 mW/cm^2 (AM1.5). The photocurrent increased from 1.6 mA/cm^2 for the cell with as-grown ITO to 3.1 mA/cm^2 for the cell with oxygen-ion-treated ITO (V_t: –60 V) and 2.2 mA/cm^2 for the cell with electron-treated ITO (V_t: 40 V). The open-circuit voltage decreased from 500 mV for the cell with as-grown ITO to 390 mV for the cell with oxygen-ion-treated ITO, in contrast to an increase in the open-circuit voltage of 540 mV for the cell with electron-treated ITO.

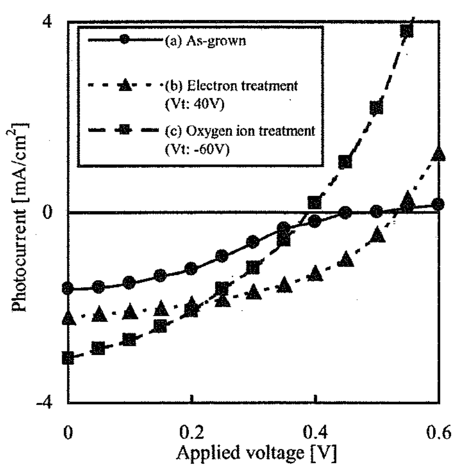


Fig. 2. Photocurrent–voltage characteristics of cells built on (a) as-grown, (b) electron treatment (V_t: 40 V), (c) oxygen ion treatment (V_t: –60 V) ITOs under irradiation intensity of 100 mW/cm^2 (AM1.5).

The effect of oxygen plasma treatment on cell characteristics was determined by measuring the photovoltaic properties of the devices formed on ITO substrates which had been treated at an applied voltage (V_t: treatment voltage) ranging from –70 to 40 V. Figure 3 shows the cell characteristics for an irradiation intensity of 100 mW/cm^2 (AM1.5). As shown in Fig. 3(a), the short-circuit photocurrent density increased markedly with an increase in the negative treatment voltage applied to the ITO substrate, that is, oxygen ion treatment. However, the open-circuit voltage and fill factor decreased with an increase in the negative treatment voltage, and they were decreased markedly by a negative treatment voltage of –50 V or more. The short-circuit photocurrent density and open-circuit voltage increased with the positive treatment voltage applied to the ITO substrate, that is, electron treatment, and the fill factor had its best value of about 0.5. The treatments by oxygen ions and electrons apparently improve the photocurrent density of the cells. We therefore focused on the increase in the photocurrent of the cells after oxygen plasma treatment.

The oxygen plasma treatment by microwave and rf plasma can be attributed to alteration of the oxidation structure in the ITO surface [7] in addition to the removal of organic contaminants. Since the work function of the ITO is increased by the oxygen plasma treatment, the device performance of OLED is improved by increased hole injection from the ITO to the HTL [7–14]. The work function of the ITO was markedly increased by oxygen plasma treatment by electron-beam-excited plasma (EBEP), as shown in Fig. 4. In the treatments due to oxygen ions and electrons, therefore, the improvement of the short-circuit photocurrent density suggests that the increase in the work function of ITO plays a role in increasing the hole injection ability at the ITO/CuPc interface. On the other hand, the open-circuit voltage coincided well with the Fermi level difference between the electrode and organic layer as reported by Miyairi and colleagues [17]. Since the Fermi level of the CuPc layer and the work function of the as-grown ITO are about 4.9 and 4.8 eV, respectively, the ITO/CuPc interface forms a slight potential barrier because the energy difference between the as-grown ITO and the CuPc is estimated to be about 0.1 eV. On the other hand, since the work function of oxygen-plasma-treated ITO is about 5.2 to 5.8 eV, the oxygen-plasma-treated ITO/CuPc interface is expected to be an ohmic contact.

The effect of the work function of ITO on hole injection was determined by measuring the current–voltage characteristics of the ITO/CuPc interface by the current

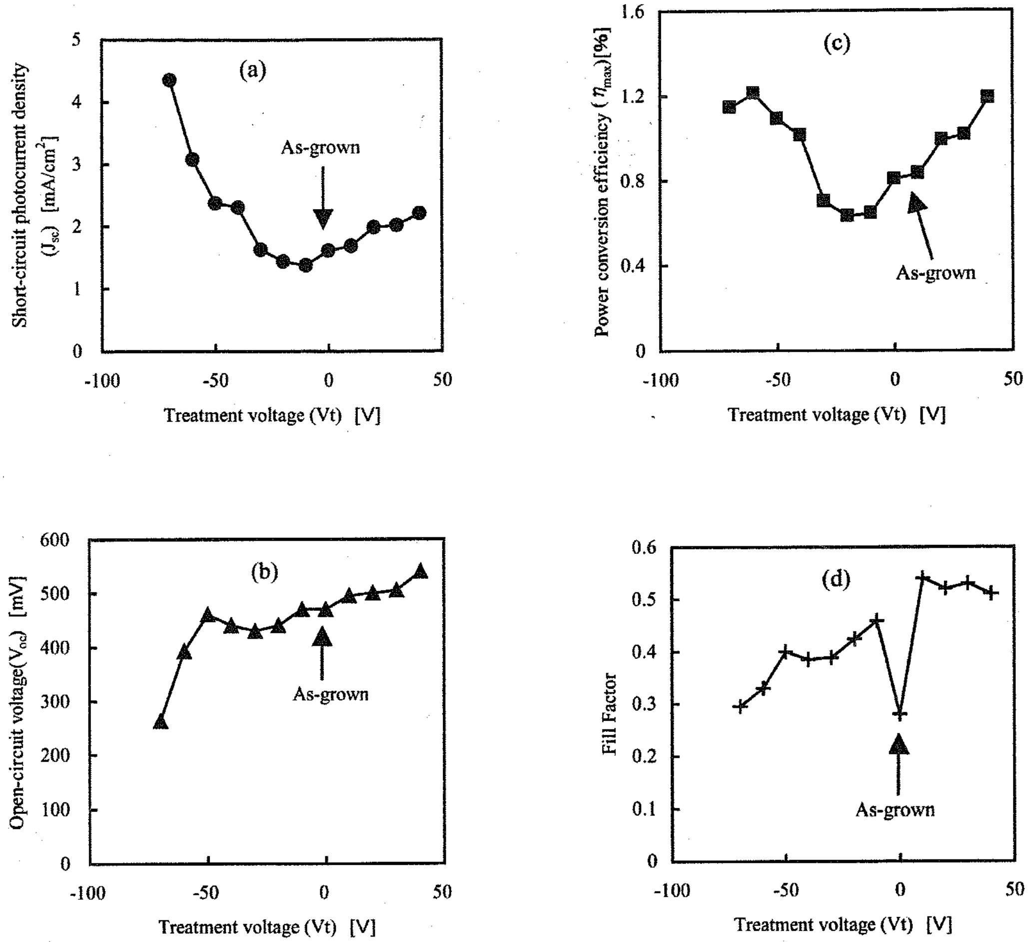


Fig. 3. Effect of treatment voltage (V_t) to ITO on cell characteristics: (a) short-circuit photocurrent density (J_{sc}), (b) open-circuit voltage (V_{oc}), (c) power conversion efficiency (η_{max}), (d) fill factor.

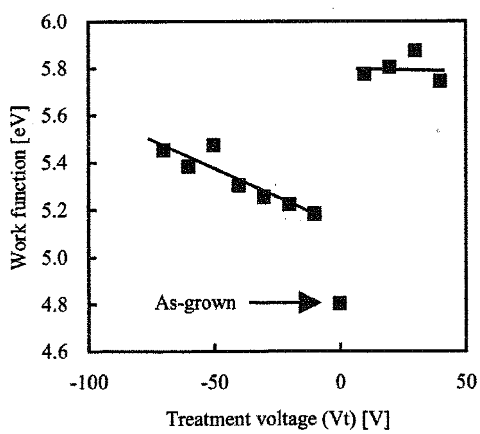


Fig. 4. Effect of treatment voltage (V_t) to ITO on work function of ITO surface.

image tunneling spectroscopy (CITS) mode of AFM. The CITS mode of AFM is a powerful tool for investigating the electronic properties of a microscopic area by modifying the AFM tip to measure the current–voltage characteristics between the tip and the specimen. We obtained current–voltage characteristics measured with the voltage between the ITO layer and the rhodium (Rh)-coated AFM tip with a radius of 100 nm adjusted from 0 to 10 V (sweep rate of the applied voltage for 20 ms). The applied voltage was about 20 times the open-circuit voltage of cell, because the contact resistance of the microscopic gold-coated AFM tip used in these experiments was large. Considering that the work function of Rh is 5.1 eV, the Rh/CuPc interface is expected to be ohmic. The obtained currents are attributed to holes through the CuPc layer and the ITO/CuPc interface. Figure 5 shows current–voltage characteristics for a CuPc layer 8 nm thick built on ITO treated by oxygen plasma. As seen in Fig. 5, the turn-on voltage of the oxygen-plasma-treated ITO/CuPc specimen is markedly reduced and the currents of the specimens with oxygen-ion- and electron-treated

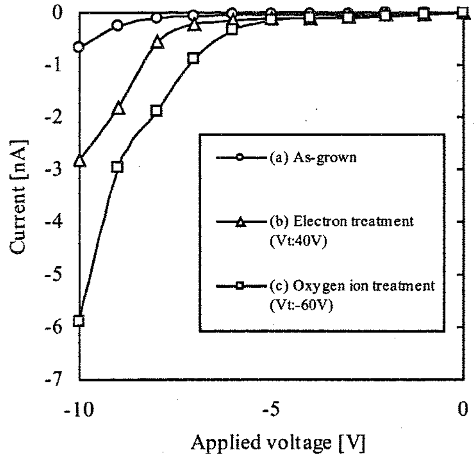


Fig. 5. Current–voltage characteristics of CuPc built on (a) as-grown, (b) electron treatment (V_t: 40 V), and (c) oxygen ion treatment (V_t: –60 V) ITOs.

ITO are increased by factors of about six and about three at an applied voltage of –10 V, respectively, compared with the specimen with as-grown ITO. Hence, the enhancement of hole injection is concluded to be due to an increase in the work function of ITO by oxygen ion and electron treatment. However, the current for the specimen with the oxygen-ion-treated ITO (V_t: –60 V) is twice that of the specimen with electron-treated ITO (V_t: 40 V).

Hence, the CuPc layer was investigated in order to elucidate the influence of ITO treated by different species, that is, oxygen ions and electrons, on the variation of crystallinity of the CuPc layer. The crystallinity of the CuPc layer was examined by XRD. The CuPc layers on ITO treated by different species have distribution patterns around $2\theta = 7.3°$, 21.7°, 30.6°, and 35.6°. The distribution patterns around $2\theta = 7.3°$ and 35.6° include a head-to-tail pattern corresponding to a stacked structure of neighboring CuPc molecules and a face-to-face pattern corresponding to a stacked structure of perpendicular CuPc molecules, respectively. Since the full-width-half-maximum (FWHM) values of both diffraction peaks decreased in the order of a treatment voltage of –60 V (FWHM of head-to-tail: 0.1°, FWHM of face-to-face: 0.11°) and a treatment voltage of 40 V (FWHM of head-to-tail: 0.33°, FWHM of face-to-face: 0.29°), the CuPc layer on the oxygen-ion-treated ITO is expected to have higher crystallinity than that on the electron-treated ITO. These experimental findings suggest that the CuPc molecules on the oxygen-ion-treated ITO are stacked with higher orientation than those on the electron-treated ITO during the growth process. Since organic layers with high orientation such as titanylphthalocyanine generally have a high conductivity [18], the increase in the current in the oxygen-ion-treated ITO/CuPc specimen, as shown in Fig. 5, may also be affected by the crystallinity of the CuPc layer. Thus, it is concluded that the increase in the short-circuit photocurrent density for cells with oxygen-ion-treated ITO is due to a lowering of the total resistance of the cell, resulting in a low potential barrier for hole injection at the ITO/CuPc interface and high conductivity of the CuPc layer.

The open-circuit voltage in the devices decreased markedly with a negative treatment voltage of –50 V or greater applies to the ITO substrate (oxygen-ion treatment). In the case of electron treatment, on the other hand, the fill factor had a high value of about 0.5. These phenomena are thought to be affected by the electronic properties at the CuPc/C_{60} interface, associated with the changes in the crystallinity of the CuPc layer described above. However, further studies are needed for confirmation of these phenomena.

4. Conclusions

We demonstrated that the photovoltaic cell characteristics improve due to the treatment energy used for oxygen plasma treatment of ITO. The short-circuit photocurrent density increased markedly with increased treatment energy of the ITO substrate. In particular, in treatment by positive oxygen ions, the photocurrent of the cell was twice that of the cell with as-grown ITO.

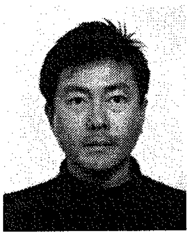
It is concluded that the oxygen plasma treatment is effective in producing: (1) a very clean surface due to the removal of organic contaminants near the ITO surface, (2) an increase of hole injection from the CuPc to ITO due to the large work function of the ITO substrate, (3) changes in the CuPc molecular configurations during the growth process, leading to high conductivity of the CuPc layer. However, further studies are needed for confirmation of the electronic properties at the CuPc/C_{60} interface and their influence on the open-circuit voltage and fill factor.

REFERENCES

1. Wöhrle D, Tennigkeit B, Elbe J, Kreienhoop L, Schuurpfeil G. Various porphyrins and aromatic tetracarboxylic acid diimides in thin film p/n-solar cells. Mol Cryst Liq Cryst 1993;228:221–226.
2. Rostalski J, Meissner D. Monochromatic versus solar efficiencies of organic solar cells. Solar Energy Mater Solar Cells 2000;61:87–95.
3. Peumans P, Bulović V, Forrest SR. Efficient photon harvesting at high optical intensities in ultrathin organic double-heterostructure photovoltaic diodes. Appl Phys Lett 2000;76:2650–2652.

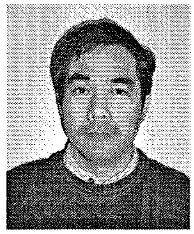
4. Peumans P, Forrest SR. Very-high-efficiency double-hetero structure copper phthalocyanine/C_{60} photovoltaic cells. Appl Phys Lett 2001;79:126–128.
5. Thelakkat M, Schmitz C, Schmidt H-W. Fully vapor-deposited thin-layer titanium dioxide solar cells. Adv Mater 2002;14:577–581.
6. O'Regan B, Grätzel M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films. Nature 1999;353:737–740.
7. Milliron DJ, Hill IG, Shen C, Kahn A, Schwartz J. Surface oxidation activates indium tin oxide for hole injection. J Appl Phys 2000;87:572–576.
8. Kim JS, Granstrom M, Friend RH, Johansson N, Salaneck WK, Daik R, Feast WJ, Cacialli F. Indium-tin oxide treatments for single- and double-layer polymeric light-emitting diodes: The relation between the anode physical, chemical, and morphological properties and device performance. J Appl Phys 1998;84:6859–6870.
9. Ishii M, Mori T, Fujikawa H, Tokito S, Taga Y. Improvement of organic electroluminescent devices performance by in situ plasma treatment of indium-tin-oxide surface. J Lumin 2000;87–89:1165–1167.
10. Sugiyama K, Ishii H, Ouchi Y, Seki K. Dependence of indium-tin-oxide work function on surface cleaning method as studied by ultraviolet and x-ray photoemission spectroscopy. J Appl Phys 2000;87: 295–298.
11. Mason MG, Hung LS, Tang CW, Lee ST, Wong KW, Wang M. Characterization of treated indium-tin-oxide surfaces used in electroluminescent devices. J Appl Phys 1999;86:1688–1692.
12. We CC, Wu CI, Stunm JC, Kahn A. Surface modification of indium tin oxide by plasma treatment: An effective method to improve the efficiency, brightness, and reliability of organic light emitting devices. Appl Phys Lett 1997;70:1348–1350.
13. Hashimoto Y, Hamagaki M, Sakakibara T. Effect of ionization potential of hole transport layer on device characteristics of organic light emitting diode with oxygen plasma treated indium tin oxide. Jpn J Appl Phys 2001;40:4720–4725.
14. Hashimoto Y, Osato Y, Tanaka M, Hamagaki M, Sakakibara T. Effect of oxygen plasma treatment of indium tin oxide for organic light-emitting devices with iodogallium phthalocyanine layer. Jpn J Appl Phys 2002;41:2249–2251.
15. Hara T, Hamagaki M, Sanda A, Aoyagi Y, Namba S. New high current low energy ion source. J Vac Sci Technol 1987;B5:366–368.
16. Pettersson LAA, Roman LS, Inganäs O. Modeling photocurrent action spectra of photovoltaic devices based on organic thin films. J Appl Phys 1999;86: 487–496.
17. Miyairi K, Ito W, Hashimoto Y. Photovoltaic properties of double layer devices consisting of titanium dioxide and porphyrin dispersed hole transporting material layer. Thin Solid Films 2003;438–439:147–152.
18. Kotani K, Muranoi T, Kikumura I, Masui M, Takeuchi M. Effects of molecular configurations on the electrical resistivity of titanylphthalocyanine thin films. Jpn J Appl Phys 1995;34:3654–3657.

AUTHORS



Yuichi Hashimoto (member) received his M.E. and Ph.D. degrees in electrical engineering from Chuo University in 1985 and 2000. Since 1985, he has worked as a research engineer at Canon Inc. His research interests include electrification and electronic properties in organic photoconductor, optoelectronic properties in organic light-emitting diodes, and deposition process in functional films as diamondlike carbon.

AUTHORS (continued)



Manabu Hamagaki (nonmember) received his B.E. degree in electrical engineering from Tokyo Denki University in 1976, and Ph.D. degree from the Science and Engineering Department, Saitama University, in 1996. The subject of his dissertation concerned electron-beam-excited plasma and its applications. His main interests are development of plasma source and plasma process.