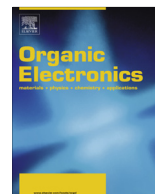




ELSEVIER

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Work function changes of plasma treated indium tin oxide

Kongduo He^a, Xilu Yang^a, Hang Yan^a, Zhonghang Wu^a, Zebin Li^a, Shaofeng Zhong^a, Qiongrong Ou^{a,b,*}, Rongqing Liang^{a,b}^aDepartment of Light Sources and Illuminating Engineering, Fudan University, Shanghai 200433, People's Republic of China^bEngineering Research Center of Advanced Lighting Technology, Ministry of Education, Shanghai 200433, People's Republic of China

ARTICLE INFO

Article history:

Received 24 February 2014

Received in revised form 30 April 2014

Accepted 5 May 2014

Available online 17 May 2014

Keywords:

Work function

Plasma

Indium tin oxide

Exponential decrease

Linear decrease

First order reaction

ABSTRACT

The work function (WF) changes of indium tin oxide (ITO) treated by O₂ or Cl₂ plasma were investigated. The WF firstly decreases in an exponential way for 2–6 h and subsequently in a linear way for days in air after plasma treatment. X-ray photoelectron spectroscopy (XPS) shows the dipole layer formed by O–In and O–O bonds in the ITO surface treated by O₂ plasma increases the WF. Exposed in vacuum, the O–O bonds tend to break and the reactive O species reduce in the oxidized ITO surface, accounting for the exponential decrease of WF. The environment preserving the chlorinated or oxidized ITO is important to slow down the decrease of WF. The mechanism for WF changes of plasma treated ITO is significant to investigate the properties of organic optoelectronic devices.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Transparent indium tin oxide (ITO) is widely used in devices such as organic photovoltaic cells [1], organic light-emitting diodes [2] and liquid crystal displays [3]. In general, a typical organic optoelectronic device usually consists of a sandwich structure with the organic thin film deposited onto the ITO-coated glass substrate and covered by the patterned top metal cathode contact. The surface properties of ITO directly affect the characteristics of devices due to the direct contact with organic films. The phenomena of unstable current–voltage characteristics have been observed in devices built on the ITO surface [4–7]. To mitigate the problems, various surface treatment processes have been adopted to modify the ITO surface properties such as work function (WF). Among those surface-modifying methods, oxidative treatments and chlorinated treatments are well-recognized as the most

effective methods for enhancing the WF of ITO [8–11]. Raising the WF reduces the interfacial barrier of hole injection from the ITO surface to organic layer. However, the effects of such treatments decrease over time. The increased WF of ITO after O₂ plasma treatment decays over time and returns to its original values within hours or months, which is considered to cause carriers unbalanced and thus affect the device reliability [12–15]. It was found that the electroluminescent intensity or luminescence of optoelectronic devices built on O₂ plasma treated or UV-ozone treated ITO decayed rapidly in the initial operating hours [7,11,16]. Possible explanations include oxidation of the organic layer by reactive oxygen species on ITO surface, crystallization of organic materials and indium diffusion into organic layers [17–19]. The decay of ITO WF may also directly affect the efficiency of hole injection and thus the reliability of devices. The cause of the WF decay is not immediately clear but may involve diffusion of surface-bound oxygen into the bulk along grain boundaries [20] and the adsorption of ambient hydrocarbon [21]. However, the underlying mechanism in terms of the WF decay still deserves further research.

* Corresponding author. Present address: Fudan University, 220 Handan Road, Shanghai 200433, China. Tel./fax: +86 21 55665636.

E-mail address: qrou@fudan.edu.cn (Q. Ou).

In this paper, O₂ and Cl₂ plasma treatments were carried out on ITO substrates to enhance the WF. The vibrating capacitor Kelvin probe (KP) method was applied to monitor the WF changes of ITO preserved in different gases after plasma treatment. Furthermore, in order to investigate the rapid WF decrease of ITO samples in the first two hours after O₂ plasma treatment, X-ray photoelectron spectroscopy (XPS) was used to analyze the surface chemistry and electronic structure. The results showed a complicated and subtle variation of the content and electronic structure of elements C and O on the ITO surface.

2. Experimental

ITO samples with 160 nm thick and 8 Ω/cm² films on glass substrates were obtained from Crystal Technologies Ltd. Before plasma modification, ITO samples were firstly cleaned sequentially in ultrasonic baths of acetone, isopropyl alcohol and deionized water for 15 min, respectively and then dried by blowing high purity nitrogen gas. The samples were labeled as “As-cl”. Then they were modified by O₂ or Cl₂ inductively coupled plasma with operating pressure of 5 Pa and an rf power of 40 W for 20 min and 10 min, respectively. After plasma treatment, all the ITO samples were preserved in different gases or measured by KP (SKP-5050, KP Technology Ltd.) in air or analyzed by XPS.

The WF changes of plasma treated ITO in air were monitored by KP measurements. This method, determining the contact potential difference (CPD) of a sample with respect to a reference, is a relative measure of WF. A gold foil was chosen as the standard sample and the WF of gold was recognized unchangeable in the period of KP measurements. The relative WF (φ) of an sample was given by

$$\varphi(\text{sample}) = e * \text{CPD} + \varphi(\text{Au}) \quad (1)$$

The WF values of As-cl ITO samples, within an error of 0.05 eV, were a little higher than the reported values, which has little effect on the study of WF decay.

XPS was employed to measure the core level spectra of C1s, O1s, In3d, Sn3d and the chemical composition on the surface of ITO samples in a RBD upgraded PHI-500C system with Mg K α X-ray radiation at 1253.6 eV. The pressure in the analysis chamber was maintained at approximately 10⁻⁵ Pa or lower. The scanning step was set to 0.2 eV. All the XPS spectra reported here were referenced to the binding energy of the C1s peak defined at 284.6 eV. After subtracting the Shirley background, the core level spectra were fitted with Gaussian peaks to identify different chemical state of C or O elements.

3. Results and discussion

Comparing with the As-cl ITO sample with WF of 4.86 eV, Figs. 1 and 2 show the WF increment changes of ITO modified by O₂ and Cl₂ plasma, respectively. The values of initial WF both increase 1 eV or above. It is obviously found the WF falls rapidly in the beginning after plasma treatment and then decreases slowly. According to the decrease trend, the curves are fitted by the combination

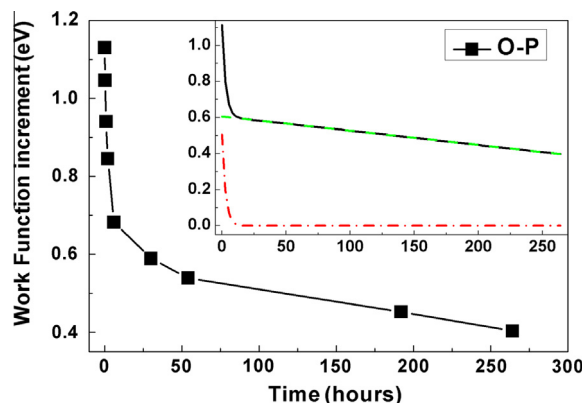


Fig. 1. WF increment changes of O₂ plasma treated ITO in air over the 270 h. The inset shows the curve-fitting result. The black solid line shows the whole fitting curve, decomposed into the green dash line for the linear part and the red dash dot line for the exponential part. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

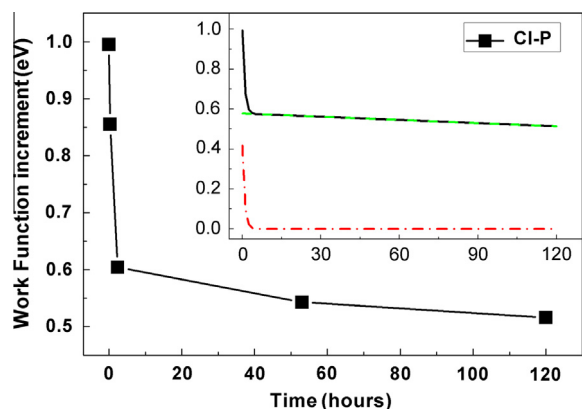


Fig. 2. WF increment changes of Cl₂ plasma treated ITO in air over the 120 h. The inset shows the curve-fitting result. The black solid line shows the whole fitting curve, decomposed into the green dash line for the linear part and the red dash dot line for the exponential part. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

of an exponential function and a linear function following as

$$y = p1 * \exp(-x/p2) + p3 - x/p4 \quad (2)$$

where $p1$, $p2$, $p3$, $p4$ are all coefficients, y is the WF increment, $(p1 * \exp(-x/p2))$ is the exponential part and $(p3 - x/p4)$ is the linear part. The fitting curves are shown in the insets of the two figures. The black solid line denotes the fitting curve which is decomposed into two parts, including the exponential part for the red dot dash line and the linear part for the green dash line. Table 1 shows

Table 1
Coefficients of the curve-fitting functions from the insets of Figs. 1 and 2.

	$p1$	$p2$	$p3$	$p4$
O-P	0.51	2.73	0.61	1266.50
Cl-P	0.42	0.84	0.58	1893.38

Download English Version:

<https://daneshyari.com/en/article/1263816>

Download Persian Version:

<https://daneshyari.com/article/1263816>

[Daneshyari.com](https://daneshyari.com)