Wet chemical surface modification of ITO by a self assembled monolayer for an organic thin film transistor

Seung Hyun Jee, Soo Ho Kim, Jae Hwan Ko, Dong-Joo Kim[a] and Young Soo Yoon*

Department of Advanced Technology Fusion, Konkuk University, 1 Hwayang-dong, Gwangjin-gu, Seoul 143-701, Korea
[a]Materials Research and Education Center, Dept. of Mechanical Engineering, Auburn University, 201 Ross Hall, AL 36849-5341, USA

Indium tin oxide (ITO), which is used as an electrode in organic thin film transistors (OTFT), was modified with a self-assembled monolayer (SAM) by wet chemical surface modification. The surface of the ITO was treated by a dipping method in a solution of 2-chloroethane phosphonic acid (2-CEPA) at room temperature. The work function in the ITO which was modified with the SAM in the 2-CEPA was 5.43 eV. The surface energy and a transmittance were unchanged within an error range. In this study, therefore, the possibility of ohmic contact is demonstrated in the interface between the ITO and the organic semiconductors. These results suggest that the treatment of the ITO with the SAM can greatly enhance the performance of an OTFT.

Key words: Organic Thin Film Transistor (OTFT), Indium Tin Oxide (ITO), Work Function, Self Assembled Monolayer (SAM).

Introduction

During the last decade, organic devices have been used in various types of electronics [1]. Hence, researchers have extensively investigated organic light emitting diodes (OLEDs) [2, 3], organic thin film transistors (OTFTs) [4, 5], and organic photovoltaic cells [6, 7]. As a result, commercial forms of these products are now extending into various markets. In particular, OTFTs, which are based on thin films of polymers or monomers, are increasingly used in commercial devices with flat panel displays [8]. However, OTFTs still have some problems, such as a high operating voltage, a low efficiency and a short device life-span [9]. To overcome these problems and to improve the performance of OTFTs, many researchers are researching organic semiconductors, gate dielectric layers and source/drain electrodes [8]. The source/drain electrode, which influences the high performance of OTFTs, has recently become an interesting research topic [9].

Hole injection at an electrode interfaced with an organic semiconductor depends on the work function of the electrode and the organic semiconductor [9]. To increase the hole injection, we must ensure ohmic contact at the interface between the electrode and the organic semiconductor [10]. Ohmic contact is achieved at the interface whenever the work function of the electrode is higher than that of the organic semiconductor. Because ohmic contact at the interface has no energy barrier, holes are injected from the electrode to the organic semiconductor. Source/drain electrodes should therefore be made of conducting materials that have a high work function in OTFTs.

Because an indium tin oxide (ITO) electrode (work function: 4.5 eV) is optically transparent in an OLED, recently, ITO is being used for the electrode of the OTFT to drive the OLED [11]. When we use an ITO electrode in the OTFT, we can save costs: that is, by using the photo masks of the OLED and the OTFT together, we can reduce the required number of photo masks.

However, the work function of ITO (4.5 eV) is lower than that of an organic semiconductor (work function of pentacene: 5.3 eV) in an OTFT. Hence, the OTFT with an ITO electrode still has some problems (high operating voltage, low efficiency, etc), although we can solve these problems by increasing the work function of the ITO.

Figure 1 shows the structure of an OTFT with ITO electrodes. To achieve the required ohmic contact, we had to ensure that the work function of ITO was higher than 5.3 eV. The work function of a conducting material is known to be influenced by the electrostatic condition at its surface [12]. Furthermore, to increase the work function and to improve the hole injection, researchers have endeavored to modify the surface of the ITO by using a plasma treatment [13] or aqua regia [14]. By using these solutions, Zehner et al. [15] and Champbel et al. [16] have recently shown that dipolar moments form a self-assembled monolayer (SAM) on gold, and that the SAM can be used to control the work function. We have shown that an ITO electrode with a SAM (2-

*Corresponding author:
Tel : +82-2-2049-6042
Fax: +82-2-452-5558
E-mail: ysyoon@konkuk.ac.kr
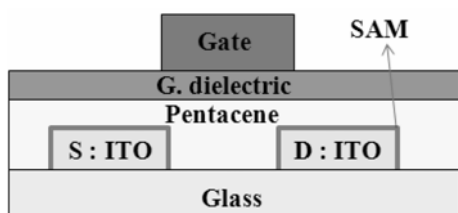
Fig. 1. Schematic diagram of an OTFT using ITO electrodes.

CEPA) can greatly increase the ITO work function without surface energy. In addition, the ITO electrode with the SAM has no visible change in optical properties.

We hypothesized that the SAM (2-CEPA) could greatly increase the work function of ITO and thereby improve the performance of an OTFT. The SAM clearly increases the work function of the ITO [17].

Experiments

We prepared ITO glasses. The ITO has a thickness of 400 Å on the glass and a sheet resistance of 20-30 Ω/□. This was measured using a four-point probe and a surface profiler (Alpha-step). We used 2-chloroethane phosphonic acid (2-CEPA) for the surface modification by a SAM. Figure 2 shows the molecular structure of the 2-CEPA on the ITO surface. The ITO glasses were immersed in a mixed solution of H_2O_2:NH_3:H_2O_2 (3:3:5) for 10 minutes to achieve good adherence of the SAM molecules on the ITO [18]. We then rinsed the glass in isooctane and dried it with N_2 gas in order to remove the mixed solution. A solution of 2-CEPA (50 μM) was prepared in 30% methanol with chloroform. The ITO glasses were then immersed in the solution for 1-23 hours. Finally, we rinsed the ITO glass in 30% methanol with chloroform and dried it with N_2 gas.

To measure the work function, the surface energy, and the transmittance of the ITO with the SAM, we used a Kelvin probe, a contact goniometer, and a UV visible spectrometer. Also, we used scanning electron microscopy (SEM) and an acidimeter to analyze the surface properties of the ITO with the SAM and the SAM solution.

Results and Discussion

We need to determine the immersion time required to
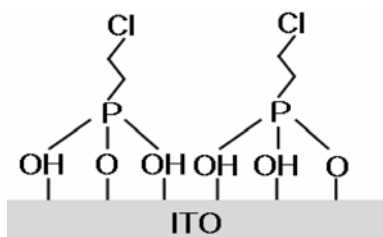
Fig. 2. Molecular structures of the 2-chloroethyl phosphonic acid (2-CEPA).

form a complete monolayer with a maximum work function. Figure 3 shows the work functions of the ITO with various periods of SAM treatment (from 1 hour to 23 hours). The ITO with a SAM shows an increase in the work function from 0.5 eV to 0.83 eV, regardless of the treatment time. We adopted a treatment period of 11 h as the saturation time because the sample with a treatment of 11 hours produced the largest work function. The cause of the increase in the work function of the ITO with an increase of the immersion time is due to the increase of the bond between SAM molecules in the solution and ITO atoms on the surface. However, when the ITO was immersed in a 2-CEPA solution for a treatment period greater than 11 h, the work function decreased. Figure 4 shows FESEM surface images of
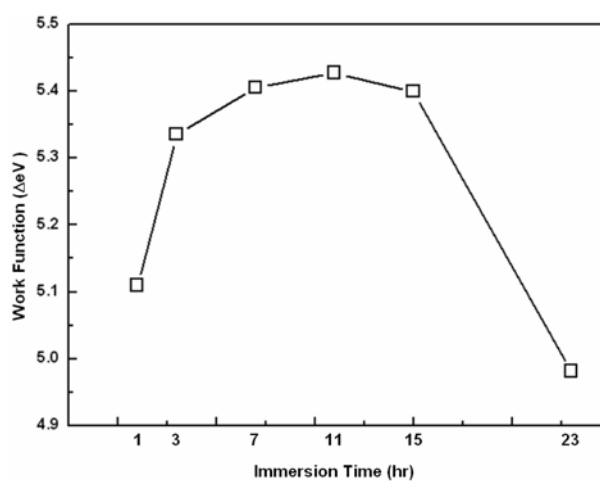
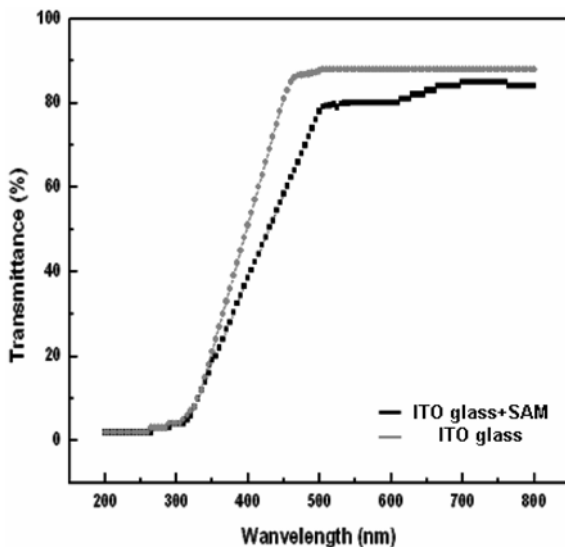**Fig. 3.** Dependence of the work function on immersion time for 2-CEPA.
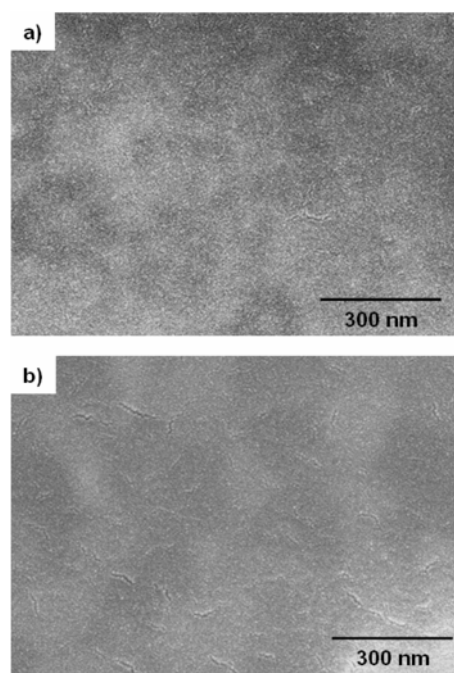
Fig. 4. FESEM surface images of ITO glass immersed for (a) 11 hours, (b) 23 hours in SAM solution.

Table 1. Contact angle and surface energy of ITO

Sample	contact angle (Diiodomethane)	contact angle (D.I. water)	Surface energy (mJ/m^2)
ITO+SAM	53°	47°	37
ITO	63°	45°	35

the ITO for samples treated with SAM for (a) 11 hours and (b) 23 hours. The SAM molecules on the ITO surface were observed by using the FESEM because the SAM is very thin and the SAM is damaged by electrical field emission in the FESEM. However, the Fig. 4(b) shows the surface of the ITO has unknown surface defects. Acidity in the solution of the SAM has pH=2.96. We expect that the solution of the SAM damages the surface of the ITO due to its acidity. The surface of the ITO has unknown defects which might increase the amount of dangling bonds in the ITO. The dangling bonds on the surface increase the number of electrons, thereby decreasing the work function in the ITO with a treatment time of 23 hours. We experiment-ally observed a 0.83 eV increase in the work function of the ITO modified with the SAM (2-CEPA). The indium, tin and oxygen atoms on the ITO surface combine with the 2-CEPA molecules after the surface modification by the SAM. The molecule combinations have a bonding strength that can restrict electrons on the ITO [15]. The work function of the ITO therefore was increased because the SAM increased the bonding energy to the surface of the ITO and restricted the release of electrons in the ITO.

The surface energy and the transmittance are also important factors in a device with an ITO. These can cause serious problems in the adhesion and the optical properties. To calculate the surface energy of the ITO treated with the SAM (2-CEPA), we used Owen's method in conjunction with the results of a contact goniometer [19]. The surface energy (γ_s) of a solid is equal to the sum of the dispersion (γ_s^d) and the polar (γ_s^p) components. That is;

$$\gamma_s = \gamma_s^d + \gamma_s^p$$

As shown in Table 1, the surface energy of the ITO, which we measured with Owen's method, was unchanged by the SAM (2-CEPA), though there was some change in the value due to experimental error. Besides, the transmittance of the SAM-treated ITO underwent a small change, although we could not observe any meaningful change in the transmittance the SAM-treated ITO in the visible range. Figure 5 compares the transmittance of the as-received ITO with that of the SAM-treated ITO.

Conclusions

The surface modification of the ITO with the SAM (2-CEPA) could provide a simple and commercial method of increasing the work function of OTFTs with ohmic contact between the ITO and the organic semi-conductor. The measurements using the Kelvin probe, the contact goniometer and the UV visible spectro-photometer indicate that the work function of the ITO increases without any change in the surface energy and the transmittance. We expect an ITO electrode with a SAM (2-CEPA) will give great potential in OTFTs and OLEDs.

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Fig. 5. UV-VIS spectra results of (a) ITO glass and (b) ITO glass with SAM.

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