

# Surface characterisation and functionalisation of indium tin oxide anodes for improvement of charge injection in organic light emitting diodes



J. Davenas<sup>a,\*</sup>, S. Besbes<sup>a,b</sup>, A. Abderrahmen<sup>c</sup>, N. Jaffrezic<sup>c</sup>, H. Ben Ouada<sup>b</sup>

<sup>a</sup> *Ingénierie des Matériaux Polymères, CNRS — Université Claude Bernard-Lyon 1, 43 Bd du 11 Novembre, 69100 Villeurbanne, France*

<sup>b</sup> *CEGELY, Ecole Centrale de Lyon, 36 Avenue Guy de Collongue, 69131 Ecully, France*

<sup>c</sup> *Laboratoire de Physique et Chimie des Interfaces, Faculté des Sciences de Monastir, Avenue de l'Environnement, 5019 Monastir, Tunisia*

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## Abstract

Wettability studies have been performed to probe the surface properties of ITO substrates, aimed to be used as hole injecting electrode in OLEDs. The elimination of organic contaminants upon the cleaning treatment (ultrasonic bath in organic solvents) leads to an increase of the free energy of the ITO surface becoming hydrophilic. The surface energy components calculated from the Van Oss model show the appearance of a basic component upon the cleaning treatment. A thermal treatment at 100 °C for 3 h leads to a decrease of the surface free energy due to surface dehydration. These properties are attributed to the hydroxides formed at the ITO surface inducing improved adhesion at the ITO/polymer interface. The ITO surfaces have been functionalised with a chloroethylphosphonic acid mono-layer to increase their stability. The appearance of an acid–base component leads to a dipolar character of the ITO surface. The formation of a compact layer of a spin coated poly(phenylenevinylene) derivative induces the shielding of the ITO basic character. The weakening of the near infrared absorption associated to ITO free carriers confirms the formation of a dipole layer at the interface with the molecular layer in contact with ITO. Improved injection properties, shown by the current/voltage characteristics, result from the interface modifications.

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## 1. Introduction

Transparent conducting oxides are commonly used as anode material in devices combining optical and electronic functions such as organic light emitting diodes (OLEDs) or organic photovoltaic cells (OPVCs). The chemical and electronic properties of mixed oxides like indium tin oxide (ITO) anodes are critical as they control carrier injection (holes) in light emitting diodes. The optimisation of the interface between ITO and the organic layer is considered [1,2] as one of the key problems to improve the performances of these new devices, because of their low stability (non-stoichiometric oxides) and poor contact with most organic materials. Clear relations between interfacial chemical interactions and charge injection have been reported but the parameters driving the final interface properties are not completely identified [3,4]. The first step to a

better understanding of these processes is to develop a treatment to clean the ITO surfaces, which will enable the determination of the oxide chemical properties. Wettability measurements provide a powerful tool to characterise the chemical functions of the ITO surface and consequently follow the efficiency of the cleaning treatment. According to Kim et al. [1] surface hydrolysis of clean ITO surfaces leads to a better adhesion of a deposited polymer layer and, as a consequence, improved electroluminescence characteristics. Donley et al. have performed XPS studies of indium oxide standards and indium hydrolysed models [2] showing that the extreme surface of ITO samples involves high concentrations of hydroxides and oxo-hydroxide species, which generally show poor adhesion of a deposited polymer layer. The stability of the hydrolysed ITO surface greatly depends of the sample environment. We have chosen a more secure route to control the ITO/electroactive polymer interface by the ITO surface functionalisation, which will be developed in a second step. Appleyard et al. [5] have in particular demonstrated the improvement of the injection

\* Corresponding author.

E-mail address: [Joel.Davenas@univ-lyon1.fr](mailto:Joel.Davenas@univ-lyon1.fr) (J. Davenas).

Table 1  
Wetting properties

H <sub>2</sub> O contact angle	Non-treated ITO (°)	Cleaned ITO (°)	Functionalised ITO (°)	Functionalised ITO/PMOX (°)
	92	74	43.9	90

properties in a semiconductor induced by the functionalisation of the ITO surface by a monolayer of chloroethane phosphonic acid. Our purpose is to evaluate the benefit of ITO functionalisation on the behavior of polymer electroluminescent diodes.

## 2. Experimental

ITO coated glass substrates have been supplied by Merck Display Technologies (MDT). The sheet resistance of the 100 nm thick ITO layers was about 20  $\Omega/$  and optical transmittance over the visible spectrum of 80%. A wet chemical procedure has been used to clean the ITO surface before deposition of an organic layer and final evaporation of the top aluminum cathode. A PPV derivative, soluble in common solvents, poly(2-methoxy, 5-octoxy,1-4-phenylenevinylene): PMOX (synthesized by the Polymer and Membrane Laboratory of the University of Monastir), was used to spin coat a thin film giving fluorescence emission in the orange region. Using the interferometric technique, the thickness of the film was estimated to 600 nm with a FTP optical probe from Sentech.

The substrates were washed in an ultrasonic bath of acetone (HPLC grade) for 15 min, followed by isopropyl alcohol (IPA) (HPLC grade) rinsing for 15 min at room temperature, before being dried in a nitrogen gas flow. The effect of ITO dehydration has been investigated by drying ITO samples in vacuum at 100 °C for some hours.

The ITO surfaces have been functionalised by dipping the cleaned substrates for 16 h into a  $10^{-4}$  M 2-chloroethylphosphonic acid solution in (30%) methanol and (70%) chloroform. Final washing was performed with a methanol–chloroform mixture of solvents to eliminate the non-grafted molecules.

Contact angles were measured by the sessile drop method with a GBX Scientific Instrument (Romans, France). The drop image was stored by a video camera and the contact angle ( $\theta$ ) was calculated by an image analysis system. Three liquid probes were used for surface free energy calculations: diiodomethane (Sigma Chemical CO — St Louis MO USA), formamide (Sigma Chemical CO — St Louis MO USA) and distilled water. Three drops were analysed on seven samples of each type. The average of left and right angles of each drop was used for the calculation of the final contact angle. Determination of the ITO surface free energy components was performed using Van Oss model [6].

## 3. Results and discussion

### 3.1. Contact angle and surface energy measurements

The effects of the different ITO surface treatments (surface cleaning, functionalisation by a molecular layer, deposition of a polymer thin film) on the wettability are summarised in Table 1.

The as-received ITO exhibits a hydrophobic behavior becoming weaker upon elimination of the surface contaminants, which generally are of organic nature. On the other side, the surface of the deposited PMOX layer is hydrophobic as expected for most polymers. Considering the surface energies in Table 2, we observe an increase of the total energy upon the cleaning treatment, which is mainly due to higher dispersive component. Clean ITO surfaces have a basic character and became monopolar with a negligible acidic component. This result is in agreement with studies performed on different commercial ITOs [7]. The basic properties of the ITO surface presumably result from the hydroxide species of the ITO surface, evidenced by Armstrong and Donley [2,8] on the basis of XPS analysis. The origin of the surface hydroxides is attributed by these authors to the easy hydrolysis of indium oxide unsaturated sites at the ITO surface. A thermal treatment in vacuum at 100 °C for 3 h however leads to a decrease of the surface free energy showing the weak bonding of these hydroxides to the ITO surface [9]. The chemisorption of small molecules to the ITO surface appears then as a way to induce stronger bonds of a post-deposited polymer layer to the ITO surface.

### 3.2. ITO surface functionalisation

Table 1 shows the lowest contact angle for ITO functionalised with a chloroethylphosphonic acid molecular layer. The surface has become hydrophilic upon molecular layer grafting. In correlation with the evolution of the contact angle with the treatment sequence, the functionalised ITO surface exhibits the highest surface energy and dispersive component. A main increase of the polymer/ITO interactions is known to result from high surface energies, inducing improved electrical contact at the anode [10]. Moreover, we obtain (Fig. 1) a main increase of the dipolar interactions due to the enhancement of the base component and increase of the acid component upon ITO functionalisation with chloroethylphosphonic acid. In conclusion, the functionalisation of the cleaned ITO surface simultaneously leads to an increase of the dispersive component and dipolar interactions contributing to the total surface energy enhancement, from which improved interfacial properties are expected.

### 3.3. Modification of the ITO electronic properties at the polymer contact

ITO exhibits an optical absorption in the near infrared due to the free carriers, which are at the origin of the conductivity of

Table 2  
ITO surface energies calculated by Van Oss model in  $\text{mJ/m}^2$

Surface energies ( $\pm 1.5$ )	Non-treated ITO	Cleaned ITO	Functionalised ITO	Functionalised ITO/PMOX
Total energy	29.3	39.5	65.2	37.5
Dispersive component	26.6	38.4	46.5	35.8
Acid–base component	2.8	1.1	18.7	1.7
Acid component	0.3	0	1.6	0.1
Base component	7.3	10.9	54.3	5.5

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