

Influence of UV Treatment on the Electro-optical Properties of Indium Tin Oxide Films Used in Flexible Displays

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Abstract—Indium-tin oxide films are deposited by low plasma temperature RF sputtering on highly flexible modification of glycol polyethyleneterephthalate substrates. The produced layers are characterized with transparency over 82 % and sheet resistance of 86.9 Ω /square. The film's conductivity was further improved by additional UV illumination from light source (365 nm), having power of 250 W. The influence of the UV exposure dose on the structural and electro-optical properties of ITO was investigated. It was established that the optimum time of illumination is 10 minutes and further UV treatment leads to polymer substrates degradation. Structural and bonds type analysis show that at longer treatment carbon atoms release and diffuse into ITO films, which worsen their electrical behavior. For the optimum UV dose the minimum sheet resistance was measured to be 19.2 Ω /square, and the maximum transparency remained almost unchanged – above 82 %.

Keywords—Flexible displays, indium tin oxide, RF sputtering, UV treatment.

I. INTRODUCTION

IN the near future the tendency, concerning display technology and information spreading systems will be replacement of the conventional papers with flexible electronic displays, which are able to be as compact, light and multiple bending as the conventional ones [1]. The researchers direct their attention to the organic materials for building of such type of flexible light emitting device on polymer substrate. Their motives are that the organic electroluminescent materials: can be easy deposited in form of thin films by simple and cheap equipment like spin-coater, atomizer or ink-jet printer [2, 3]; can be deposited on flexible substrates at lower temperatures than the substrate's melting point [4]; have their own light emission and generate brighter light in comparison with LCD displays for example [5].

Especially crucial moment is the formation of the first element on which the structure grows further – this is the conductive transparent electrode on the front panel. Indium-tin oxide (ITO) thin films prepared by different vacuum sputtering techniques (DC, RF, and magnetron) are the most

used for this purpose [6,7]. For the proper work of the display it is accepted the transparent electrode to have sheet resistance around 50-70 Ω /square and transmittance for the visible light – at least 85-87 %. Many authors have reported sputtering of ITO on hardens polyethyleneterephthalate, acetate sheets, polystyrene substrates [8,9], but they have relatively high melting point (above 120-140 °C), which doesn't impose modification of the deposition modes in such a way to prevent the substrates from thermal deformations. Besides those authors doesn't comment also the adhesion of the films after bending of the substrate. It is known that these classes of materials and their derivatives have restricted bending abilities, because they are additionally hardened and their transparency is not high enough. Maybe this is the reason in the reports to present values not higher than 84%.

Our goal is to deposit ITO film by RF sputtering onto highly flexible glycol modification of polyethylene terephthalate (PET), which however has lower melting point. This imposes deposition at lower sputtering power (temperature) and leads to amorphous film formation with higher resistance than it is necessary and than it is usually observed at polycrystalline ITO for glass monitors. We supplied ultraviolet (UV) treatment on the prepared samples PET/ITO to reorganize the film's structure and thus to decrease its sheet resistance to the minimum possible value. This will allow ITO film to serves as effective injecting electrode in the future flexible display. We investigated the influence of the UV dose (power and duration of illumination) on the main electro-optical properties of the ITO films.

II. EXPERIMENTAL

Sheets from glycol polyethyleneterephthalate foil (PET), having melting point of 80°C, were cut with sizes 2.5 cm x 2.5 cm and were cleaned by chemical and mechanical method. Detergent solution consisting of mixed hydrogen peroxide, ammonia and distilled water in ratio 1:1:3 was prepared as addiction of the ultrasonic treatment in ultrasonic cleaner. The substrates were cleaned in it for 90 seconds. ITO films were prepared in a RF vacuum sputtering system A400 VL (Leybold Hereaus), with mounted target made from In_2O_3 and SnO_2 at a weight proportion of 95:5 mol%. The sputtering power supplied to the target was decreased in comparison with our previous developed technology for electrode on glass, where the sputtering power was kept at 220 W [10]. Here, the RF power was set to 60 W (target voltage 500 V and plasma

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current 120 mA) at deposition time of 20 minutes. The was evacuated to 8.10^{-6} Torr, the oxygen pressure was fixed to 2.10^{-4} Torr and the total pressure of reactive gas and sputtering inert (argon) gas was maintained at $2.5.10^{-2}$ Torr. In this way the substrate temperature during film growth was lower then the temperature of PET's mechanical deformation. To decrease the specific and the sheet resistance, the samples were treated with ultraviolet light (365 nm) form exposure source, having power of 250W for 10 min. Segments patterning of the ITO was performed by standard photolithographic process and etching in oxalic acid.

The thickness of ITO film was measured 148 ± 1 nm. The refractive index, extinction coefficient and physical thickness of the films were determined simultaneously from transmittance and reflectance spectra of the sample deposited on transparent substrates (optical glass) and the reflectance spectra of the corresponding films deposited on opaque silicon substrates. The spectra were recorded by a high precision Cary 5E spectrophotometer at normal light incidence in the wavelength region $\lambda = 400 - 800$ nm, with an accuracy of 0.1 and 0.5 %, respectively. The previously developed three-step algorithm was used for reliable isolation of physically correct solutions and for high accuracy determination, for instance, $\Delta d = \pm 1$ nm. Detailed information about the thickness measurement method and transmission measurements could be found in [11]. Transmittance spectra were recorded by UV-VIS Specord equipment. More details about the spectrophotometrical measurements could be found in [12]. The specific and sheet resistances of the films were measured before and after UV treatment by four-point probe FPP 500. The film structure was characterized by X-ray diffraction (XRD) using a diffractometer model PX160. Ni-filtered Cu α radiation was used at 35 kV and 15mA with $\lambda = 0.154184$ nm. For bonding type identification FTIR spectroscopy analysis was performed by Shimadzu FTIR Spectrophotometer IRPrestige-21 in reflection mode. The concentration of the charge carriers escaped from the activated traps was calculated based on conductivity measurements with Keythley 6485 picoamperimeter. The equipment for activation of the traps is "home-made" and detailed information about is can be found in [13]. Picture of the structured ITO layers on the flexible substrate is also shown.

III. RESULTS AND DISCUSSION

Decreasing of the specific sputtering power is necessary during indium-tin sputtering for prevention of the flexible PET substrate from melting. The produced ITO film is clearly amorphous as can be seen from the X-ray diffractograms (Fig. 1). The possible reason is lower energy of the sputtered particles, which doesn't possess impulse to self-organize and occupy appropriate energetic place by movement onto the substrate surface. In this way disordered ITO film grows. The sheet and specific resistance for such types of layer structures are measured by Van der Pauw technique and they are presented in Table I. The question here is how to introduce energy in the system enough to cause reorganization of the particles in lattice configuration and in the same time to avoid

overall increment of the temperature. This is possible if there is no heating component in the treating method. This is our motivation to choose to irradiate the samples with electromagnetic wave lying far away from the infrared range – namely UV exposure. After certain time of illumination reorganization of the structure occurs and crystalline like formation cause specific peaks to appear in the XRD spectrum. The strongest peak around $2\theta = 28^\circ$ can be ascribed to orientation of the formed crystals preferentially in (222) direction [14]. These peaks are actually caused by scattering of the X-rays from the grain boundaries. It seems that the sheet resistance is in reverse dependence with the degree of crystal formation (i.e. UV exposure time). However there is a limit in the exposure time at constant power, after which the ITO film's conductivity begins to worsen vastly. The peaks around 45° and 55° are due to the substrate. At no UV treatment there is no texture of the film, which can be seen from the lack of diffraction spectra in the XRD investigation.

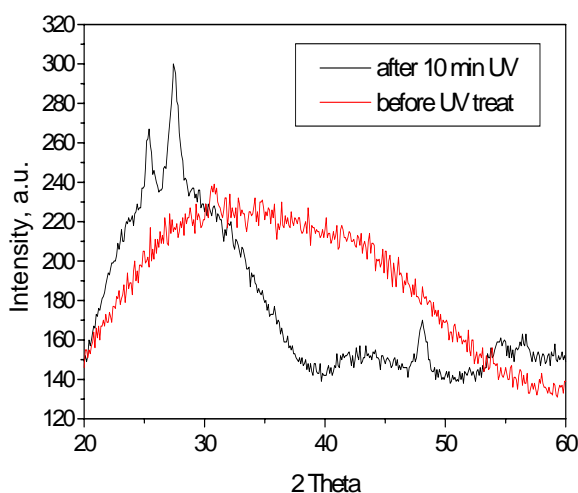


Fig. 1 XRD of ITO sputtered on PET before and after 10 minutes UV treatment

The problem can be detected using Fourier Transform Infra-Red (FTIR) spectroscopy, where attack occurs by braking of bonds activated by the UV radiation and leading to formation of carbonyl groups escaped from the polymer chains and predominantly from the aromatic rings of PET. UV causes a photochemical reaction within the polymer structure, which affects the infrared spectrum. FTIR spectra measured before and after UV treatment with different doses shown the concrete changes (Fig. 2).

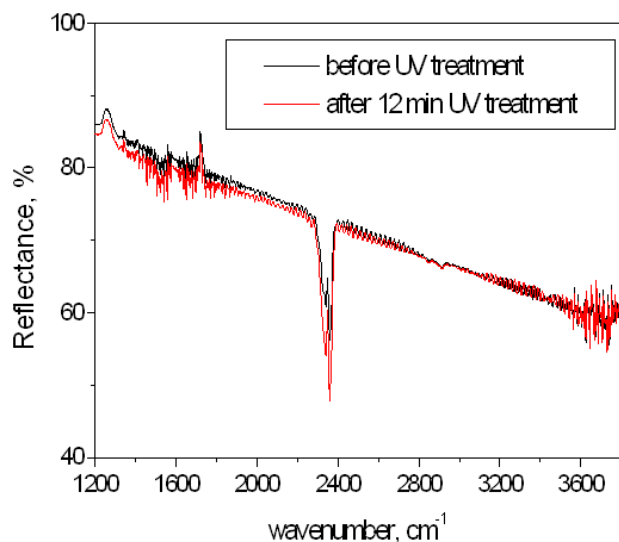


Fig. 2 FTIR of ITO sputtered on PET before and after different doses of UV

It is known that relatively good UV resistance have fluoropolymers, because they have stronger carbon-fluorine (C-F) bond (approximately 3 times higher than the carbon-hydrogen (C-H) bond), which surrounds the carbon (C-C) backbone and build up protection. In contrast with this the used modification of PET consists of many C=O and C-H₂ bonds, which is precondition for easy photo-oxidation. It seems that the desired effect of UV radiation on the sheet resistance is limited to 10 minutes of exposure. Longer time makes the resistance to increase abruptly, as can be seen from Fig. 3, because of the higher doses of introduced UV energy, causing substrate damages. The concentration of the released carbon is relatively small, but it seems that is high enough to change the films properties. This conclusion can be made, from the middle in magnitude absorption band, corresponding to the carbon in the FTIR. Around 1700 cm⁻¹ there is a clearly seen peaks corresponding to nonconjugated carbonyl groups, which presents in the layers of ITO, probably by diffusion after pretreatment. The peaks around 1300 cm⁻¹ indicate interaction between released carbon and oxygen from indium-tin oxide film in C-O-C formations and their vibrations. The lines between 450 and 1020 cm⁻¹ identify the indium-tin oxide bonds configuration and confirm the existence of In-O-In interaction, which is in good agreement with the results, reported in the literature [15].

At lower doses (shorter time than 10 minutes), the electrical behavior of the treated ITO layers can be ascribed to the activation of defects presents in the disorder matter which have captured charge carriers. The trapped carriers are escaped after vibrational interaction with the electromagnetic wave and make the sheet and specific resistance to decrease (Fig. 3). All data about the resistivity and the concentration of the free charge carriers are presented in Table I.

It was established that although the transition of the film structure to crystalline the transmission of the visible light (transparency) was not changed, as can be seen from the measured UV-VIS spectra (Fig. 4).

TABLE I
SUMMARIZATION OF THE ELECTRICAL PARAMETERS OF ITO FILMS BEFORE AND AFTER UV TREATMENT WITH DIFFERENT DURATION

	Before UV treatment	After 8 min UV treatment	After 10 min UV treatment
Rs, Ω/square	86.9	22	19.2
ρ, Ω.cm	0.175	0.282	0.241
n, cm ⁻³	1.10 ¹⁷	3.10 ¹⁹	7.10 ²¹

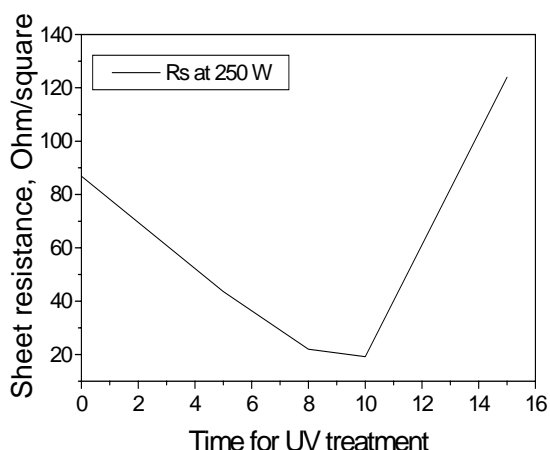


Fig. 3 Sheet resistance of ITO sputtered on PET as a function of the UV illumination time

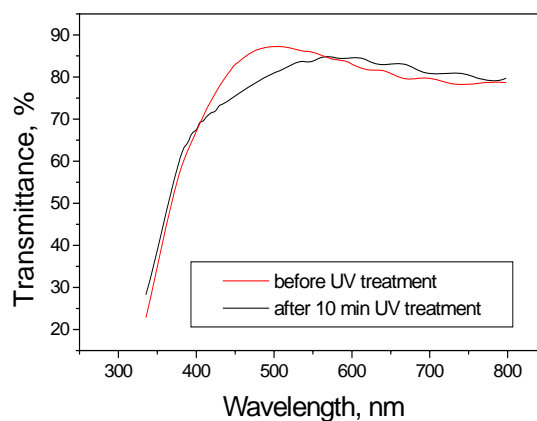


Fig. 4 UV-VIS of ITO sputtered on PET before and after different doses of UV

The consequences from the UV illumination can be taken into account during photolithographical patterning of ITO layers for pixel formation or for seven segment digits configuration for indication. This technological operation is connected with spin-coating deposition of photosensitive film (photoresist), alignment of photomask containing the desired

pattern and exposure the photoresist through the photomask with UV light up to 1 minute (according to the photoresist thickness) to change its solubility and finally etching of ITO. This means that during the improvement of the injecting properties of the transparent electrode, it must be provided some time reserve, so the total time for treatment and photolithographical exposure to be less than 10 minutes.



Fig. 5 Photo of the real structure, patterned by photolithographical process on the polymer sheet

IV. CONCLUSION

Large ITO films were deposited by RF sputtering on highly flexible modification of PET substrate at low sputtering power. The produced layers had the necessary qualities for application as electrode in flexible displays, but the resistance was still relatively high and there was a danger to cause poor charge carrier injection. This imposed additional treatment with UV light for reorganization of the ITO particles from disordered to slightly crystalline and to additionally decrement of the resistance. For 250 W power of the exposure source at 365 nm, it was found that the optimum time for UV treatment is 10 minutes. The minimum sheet resistance in this case was 19.2 Ω /square, and the maximum transmittance of the visible light remained unchanged – above 82 %. These results are useful for the future fabrication of organic flexible display, which will contain low-molecular weight electroluminescent materials deposited by spray deposition and screen printing as novel approaches for deposition of organic crystals.

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