Deposition of Transparent Electrodes for the Future Generation of Flexible Displays

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Abstract – **Indium tin oxide transparent films with thickness 58 nm were deposited by modified method for radiofrequency vacuum sputtering on flexible substrate for application as display electrode. Amorphous and colourless polyethyleneterephtalate foil (APETF), having melting point of 80 °C, was chosen as flexible substrate. The oxygen partial pressure, varying during the sputtering with one order of magnitude (1.10^{-3}-2.10^{-4} Torr), strongly affects the film structure. Another important parameter is the post deposition exposure with UV light. This treatment leads to decreasing of the sheet resistance from 359 to 68,6 Ω/square. The changes in these conditions also result in changes of the transmission for the visible light - the maximal transparency is in the range 71% to 89%. The samples were fully characterized by scanning electron microscopy, Fourier transform infrared spectrophotometer, refractive index, UV-VIS and Van der Paul sheet resistance measurements.**

Keywords – **Flexible displays, Indium-tin oxide films, RF sputtering.**

I. INTRODUCTION

During the last decade the organic materials are intensively investigated because of their potential application in displays, solar cells, sensors and other types of optoelectronic and microelectronic devices [1]. The highest attention attract the electroluminescent light emitting displays, which tent to replace the current developed liquid crystal technology (LCD) as portative flat displays, because of the lower consumption, wider viewing angle and higher own brightness. According to the contemporary initiatives for environment protection by saving paper (and preserve trees), the idea for electronic papers appears – cheep digital displays, based on organic materials, deposited on flexible substrates, bended and put in the pocket. The first step toward the physical realization is the deposition of electrode, which injects the necessary charge carriers in the organic semiconductor to cause light emission and in the same time it is enough transparent for the visible light. The most suitable and studied material is indium-tin oxide (ITO), which is usually prepared by techniques like vacuum electron beam evaporation, vacuum reactive sputtering, spray pyrolysis [2,3]. Unfortunately the temperatures developed during those processes are higher then the melting point of the substrate, so alternative technological mode must be created.

There are several reports in the literature connected with different approaches for ITO deposition on different types of flexible substrates like crosslinked hydroxypropylcellulose [4], polypropyleneadipate [5] and polyethersulfone [6]. More of the cited substrate materials are heat resistant in the temperature range Ts = 110–170°C. In some of the papers, where PET substrate is used [7] there is no data about the adhesion of the obtained ITO films and there is no information about the possible microcracks in the film during folding.

The new moment in our work is the modification of the sputtering mode in such way that we could achieve comparable parameters with those, obtained on glass substrate, without damaging of the flexible one. The efforts are directed to ITO deposition by varying the oxygen concentration in the vacuum chamber at decreased RF power. In contrast to the known values for the parameters of ITO films grown up on PET foil by vacuum deposition types of processes, here we decreased the thickness of the electrode more than twice [8], but we still kept the parameters in the same ranges as at higher thickness, which is a big advantage. The decrease of the thickness is expected to lead to higher resistance and lower mechanical stability of the film. However, we proved that at suitable deposition conditions and post deposition treatment we can keep the parameters at the desired values and thus we guarantee high quality preparation of electrodes for thinner and lighter displays.

II. EXPERIMENTAL DETAILS

Sheets from amorphous polyethyleneterephtalate foil (APETF), 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 consists of hydrogen peroxide:ammonia: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 by a RF reactive sputter system using a target with contents In_2O_3 and SnO_2 at a weight proportion of 95:5 mol%. The sputtering power input to the target was decreased in comparison with our previous developed technology for electrode on glass, where the target voltage was kept at 210 W. Here, the RF power was set to 60 W (target voltage 500 V and plasma current 120 mA) at deposition time of 20 minutes. The base pressure was 8.10^{-6} Torr, the oxygen pressure varied between 1.10^{-3} and 2.10^{-4} Torr and the total pressure of

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reactive gas and sputtering inert (argon) gas had constant value of $2.5.10^{-2}$ 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 form exposure source with power 250W for 15 min. Segment structuring of the ITO was performed by standard photolithographic process and etching in oxalic acid.

The thickness of ITO film was measured 58 ± 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 [9,10]. 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 [11] was used for reliable isolation of physically correct solutions and for high accuracy determination, for instance, $\Delta d=\pm 1$nm. 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 using four-point probe FPP 500. For composition identification FTIR spectroscopy analysis was performed by Shimadzu FTIR Spectrophotometer IRPrestige-21in reflection mode. Layers morphology was observed on Scanning Electron Microscopy JEOL - JXA733 with accelerating voltage 25 kV. Picture of the structured ITO layers on the flexible substrate is also shown.

III. Results and Discussion

After series of experiments at different deposition conditions we established that the optimal values are as they are described above. Our starting point was the lowest tension in the system ITO film/flexible substrate and to save the substrate from the plasma heating. We set the supplied RF power and argon sputtering gas concentration as constants and the oxygen reactive gas concentration as parameter. We had to set the proper concentration, so a compromise to be achieved between transparency and conductivity for the ITO film, which will perform double function in the future display – injecting electrode and viewing electrode. On the following Fig. 1 we have shown the transmission spectrum for the two boundary states: the best and the worst case of oxygen concentration. The reference curve of the transmittance for uncovered APETF is also shown on the graph as a comparison. At the low value the transparency doesn't exceed 68%, but for the higher value it achieves 88%. However for this transmittance the initial conductivity of the film was too poor. The minimal sheet resistance before exposure with UV radiation was 359 Ω/square. That's why we had decided to choose intermediate oxygen pressure value of 4.10^{-4} Torr, with average transparency of 76% and sheet resistance of 510 Ω/square, and further to decrease the resistance's value. The reason for the poor conductivity is the decreasing of the RF power, which leads to producing of amorphous film, with undefined structure. The micrograph on Fig. 2 shows the result of the scanning electronic microscope at low power and the working oxygen pressure before and after UV exposure at one and the same magnification of 4300. We had to introduce additional energy to reorganize the particles in the film and made the structure three orders of magnitude higher conducting. This may happen with ultraviolet exposure source, where the heating infrared component is rejected and there is no danger for the flexible substrate's to be damaged. It can be seen the amorphous structure without content of any microcrystals before treatment and beginning of micrograins formations after treatment. The corresponding minimal sheet resistance before exposure was 359 Ω/square, but after 15 minutes of illumination it decreased to 68,6 Ω/square. For our chosen working pressure it was 74,5 Ω/square (see Fig. 3). For comparison in the literature the typical achieved values are 160 Ω/square on (RF power = 30W, $P_{o2} = 3.10^{-3}$ Torr) [7] and even 4.104 Ω/square (RF power =100 W, Po_2 = 1 Torr) [4] on BDI Hydroxypropylcellulose cross linked with 1,4-Diisocyanatobutane substrate. The resistance is average value from measurements conducted in three different points all over the area of the substrates. The corresponding transmittances in the visible range for the cited papers are 80% for both investigations. The order of the film's thickness is also comparable – 30 and 60 nm. From the SEM observations it could be seen that there are no micro-cracks in the amorphous layer while for the UV treated sample the image represents grain boundaries.

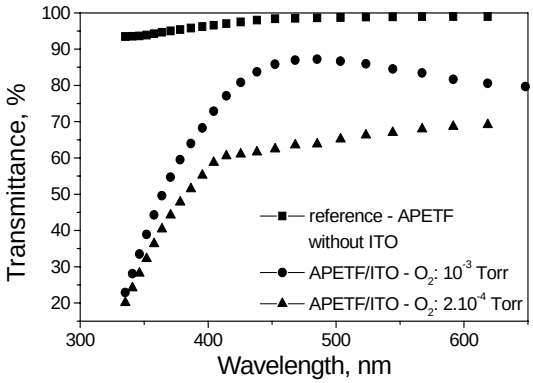

Fig. 1. UV-VIS spectra of systems APETF, APETF/ITO at partial pressure 10^{-3} Torr and 2.10^{-4} Torr.

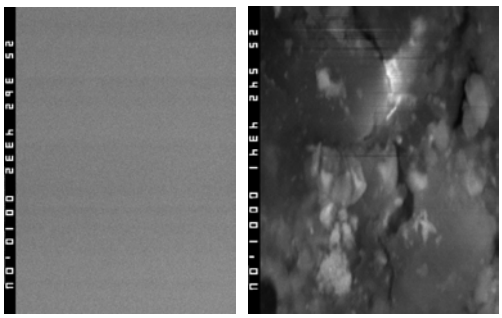

Fig. 2. SEM of untreated with UV (left) and treated with UV (right) ITO surface.

The refractive index is stable and constant in wide range of the wavelengths in the visible spectrum (see Fig. 4). It is lower than the typical measured value [13]. The possible reason is that the light propagation is easier, because the film structure (as well as the flexible substrate's structure) is not defined in certain crystal cells, but it is in form of starting stage of arrangement of non-uniformly distributed nuclei or start of micro-grains formations.

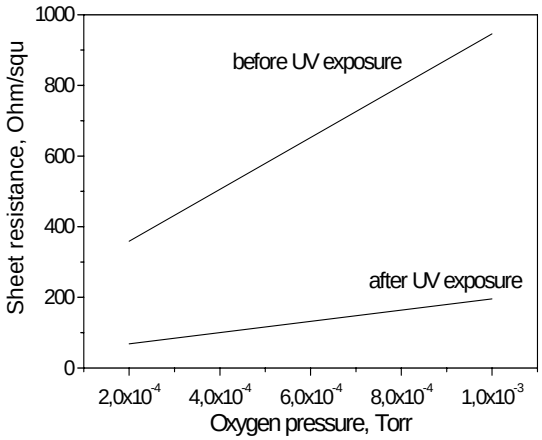

Fig. 3. Sheet resistance of the thin ITO film for different oxygen pressures, including the highest and the lowest possible values.

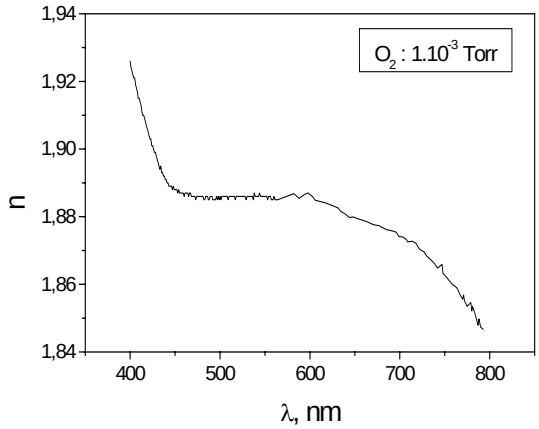

Fig. 4. Refractive index of sample prepared at partial pressure.

Typical FTIR spectra in reflectance mode, acquired in the range 300-4000 cm^{-1} for films deposited on PET at different post-deposition conditions are shown in Fig. 5. The reason for the choice of reflectance mode is that the polymer substrate and the ITO film are not transparent for the infrared (IR) light. After 500 cm^{-1} there are no specific changes in contrast to the values described in the literature, where the characterized peaks are situated between 1000 and 4000 cm^{-1} [14]. It could be seen that the character of the bonds is almost not affected by the UV exposure. The absorption is slightly higher, but the peaks are situated at the same positions, which is prove for preservation of the typical features of ITO film. The peaks situated around 430 cm^{-1} and 560 cm^{-1} confirm the existence of In-O-In bonding, which is in good agreement with the results, reported in [15]. The Sn-O and Sn-O-Sn bonds, which are usually evidenced by peaks situated around cm^{-1} and 616 cm^{-1}, are not observed here.

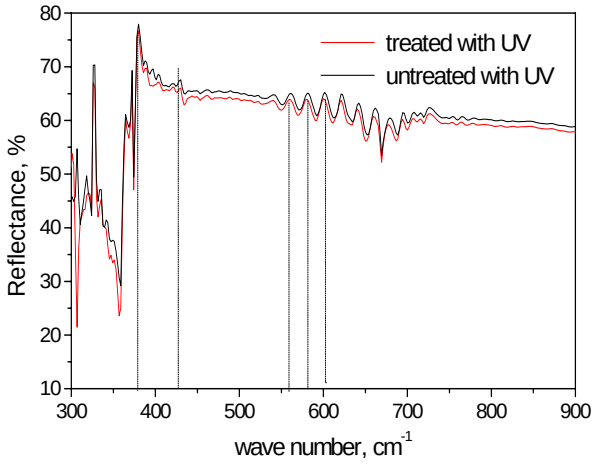

Fig. 5. FTIR spectra of the sputtered ITO layers on flexible APETF substrate before and after UV treatment.

The results show that the behavior of the film can be ascribed to "bending mode", where dipole moment or charge imbalance in the molecule occurs.

According to the measured results the IR reflectance in the range 500 - 2000 cm^{-1} is high (average 43.68 %), which is advantage for another application, different than display – this is so called heat mirror, used as element in the "smart windows".

IV. Conclusion

ITO films were deposited on flexible polymer substrate by using modified method of RF reactive sputtering at different oxygen concentrations. The obtained films have higher than 80 % transmittance, but also resistance higher than 300 Ohm/square. This was the reason to apply UV exposure for self assembly of the ITO particles after deposition. The result was 5 times decreasing of the resistance and almost no changes in the transmittance, as can be seen from UV-VIS spectrum. The UV light doesn't change the molecular structure of the film, which is proved by FTIR measurements. Its influence consists of structure's reorganization in form of microcrystals, shown by SEM observations. After deposition the PET substrates are stable and don't reveal mechanical tensions, which is evident for the ITO film's uniformity with lack of cracks and from the substrate flatness. This is the main advantage of the used modified low power sputtering technique, because of the low substrate temperature at the deposition process. During the conducted measurement another suitable application of the produced ITO films was found, because of the IR reflective properties – the heat mirrors.

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