Flexible Thick Film Electroluminescent Devices: Influence of the Mechanical Stress on Layers Behavior

Mariya Petrova Aleksandrova, Svetozar Krastev Andreev, Ivelina Nikolaeva Ruskova and Georgi Hristov Dobrikov

Abstract - **The influence of the mechanical bending on flexible screen-printed organic light emitting devices upon their electrical properties has been examined. Our measurements showed that flexible printed coatings can be bent to small radii (5 mm and 2.5 mm) of curvature and still function, despite the increase of the electrical resistance of the electrodes from 45 to 62.1 Ohms/sq. This is ascribed to the mixture of two classes organic compounds (low molecular weight and polymeric) in suitable ratio, which guarantee high adhesion and stability against strain. Device failure is caused mainly by the transparent indium tin oxide (ITO) electrode that is not resistant to continuous bending at radius 5 mm, as well as to repeated bending over 2 000 that lead to cracks occurring. Internal stress induced in organic electroluminescent layers with different thickness was determined to be in the range |1|-|7| MPa, based on the radius of curvature. Current-voltage characteristics clearly show the limit of bending, at which current flow stops, because of electrodes degradation.**

Keywords – **Flexible OLED, Thick Films, Electroluminescent Coatings, Mechanical Stress**

I. Introduction

Large-scale display production of all modern visualization devices, such as light emitting devices (inorganic LED or organic OLED) [1,2], electrochromic [3], etc. is accomplished by thin film deposition processes. In the same time the screen printing technology has offered highly reproducible and relatively inexpensive way to produce different electronic devices, such as different sensors and even solar cells [4,5]. Thick film technology is useful for deposition of highly temperature stable organic electroluminescent structures, standing work at maximum brightness for hours, which is hard achievable for thin film OLEDs [6]. The screen printing process includes patterned deposition of inks and solders mostly onto planar substrate by pressing the paste through a laser cut metal stencil or polyester screen mesh [7]. The composition for electroluminescent inks includes a light-emitting fine powder or granular material, binding substance, and a solvent. After deposition, temperature treatment is supplied for full solvent evaporation for a certain time depending on the coating thickness. Annealing temperature depends on the materials specific features – for example substance's thermal degradation or substrate's degradation point.

Existing papers in the literature about screen printed organic inks for display applications are assigned for glass substrates [8,9]. However, recently flexible devices and in particular displays have entered into the modern life and tent to improve all the time in the meaning of performance [10]. Main building coatings should be investigated for the impact of mechanical stress on their electro-optical behavior. There is information concerning this problem, but it is related to flexible thin nanometric films based OLED [11]. By our knowledge there are still no data provided for mechanical behavior of thick film flexible OLEDs. In this paper we used polyethylenetherephtalate (PET) flexible substrate covered by ITO transparent electrode and screen printed poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV):polystyrene ink and aluminum electrode to investigate stability of the organic electroluminescent device in term of electro-mechanical properties.

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II. Experimental Section

Sheets from polyethyleneterephtalate foil (PET), having degradation point of 90^{o}C, were cut with sizes 4 cm x 4 cm and were cleaned by ethyl alcohol in ultrasonic cleaner. The substrates were cleaned in it for 90 seconds. Indium tin oxide (ITO) transparent electrode films were prepared in RF vacuum sputtering system, from target consists of In_2O_3 and SnO_2 in a weight proportion of 95:5 mol%. The sputtering power supplied to the target was set to 60 W (target voltage 500 V and plasma current 120 mA) at deposition time of 20 minutes for 200 nm film thickness. The chamber was evacuated to 8.10^{-6} Torr, then the oxygen pressure was fixed at 2.10^{-4} Torr and finally 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 exposed to ultraviolet light (365 nm, 250W) for 10 min.

Soluble modification of low molecular weight electroluminescent compound 8-hydroxyquinoline aluminum salt (Alq) was mixed with polyvinilcarbazole and binder polystyrene in a suitable ratio, and then the mixture was dissolved in chloroform until viscous liquid (ink) is formed. Prepared ink was stirred one hour to increase its homogeneity. Fine meshed screen with preliminary lithographed patterns was used for screen printing of the ink. Polyurethane squeegee was used for distribution of the electroluminescent ink through the meshed screen. According to our screen pattern, 8 samples can be prepared during one deposition cycle (one squeegee movement). Principle of the screen printing process for thick film deposition is shown in fig. 1.

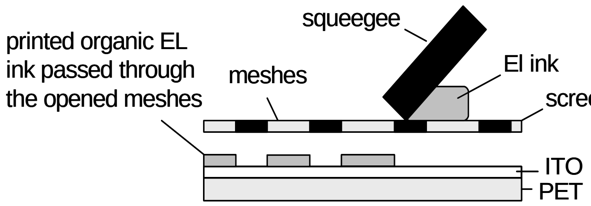

Fig. 1. Screen printing of organic electroluminescent ink.

After deposition of the coating the substrates were dried at 60 ^{o}C for one hour to ensure full solvent evaporation and binder strengthens. This results in uniform film formation, having thickness of 25 μm, measured by profilometer KLA Tencor Alpha Step100. Finally aluminum thin film (200 nm) was thermally evaporated at base vacuum 10^{-5} Torr for cathode electrode. Continuity of the coatings (or cracks in them) was monitored by optical microscopy at magnification 250. The samples were subjected to mechanical bending in static and dynamic mode. At static mode they were tested at different curvatures of folding – 10 and 5 mm in diameter respectively, standing in this position for one hour to check the steadiness of the layers at different strains. The screen printed layer was out the imaginary circle of bending. At dynamic mode frequently applied vibrations (30Hz) with intensity 35 N were supplied to the substrates for studying of the device's mechanical and electrical behavior when repeating and long term loading is applied. Changes in the sheet resistance were measured by four point probe setup. Current-voltage measurements were conducted by ampermeter Keithley 6485.

III. Results and Discussion

The film roughness was characterized before bending and average value approximately 4.6 μm for thickness of 25 μm was measured (Fig. 2). Non-uniformity in the surface's profile is probably due to scanned area, corresponding to edge of the pattern from the screen and leading to particles heaping and abrupt change in the relief. The surface is not as flat as in the case of thin film surface, because larger particles pass thought the mesh. Normally, drying process causes the ink to liquefy and bigger particles to fuse. However, here there is additional binder polystyrene that solidify too fast the ink before fusion process to happen. That's why additional planarization is necessary before aluminum electrode deposition. Used approach here, is deposition of several sprayed layers from the same ink, but highly diluted in the same solvent.

The revealing of cracks in the electroluminescent screen printed layers was monitored as a function of the bending radius of the samples (Fig. 3 a-c).

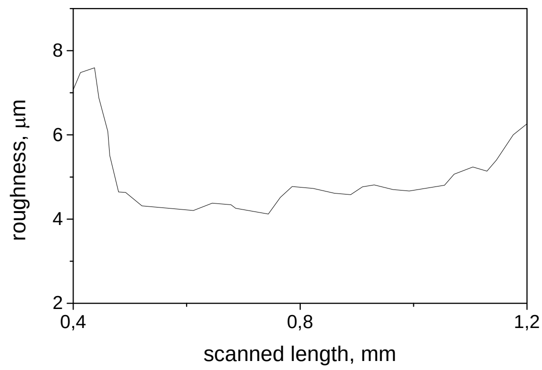

Fig. 2. Profile of the screen printed electroluminescent layer's surface.

After the weaker loading, the first several cracks occur as defect sites in the ITO thin film, they propagate and cover almost the whole sample width at the stronger load (Fig. 3d). Fig. 3 a) shows that some partially dissolved microparticles exist on the layer surface, but they are uniformly distributed on the whole area and in general the film can be considered as regularly formed. In fig. 3b can be seen some bigger fractions of organic material at 5 mm radius of curvature, but it can be clearly seen that the organic layer is continuous and no cracked, probably due to the additionally introduced polymer binder, playing a role of adhesive. The possible reason for this arrangement can be breaches in the underlying ITO film, which try to come up, because this is the bending direction. In fig. 3c obviously breaks in the organic layer initiate to appear after bending at radius 2.5 mm for 1 hour. They can be noticed as white spots in between the organic particles, so this is the limit of bending of the flexible sample.

Fig. 3d shows separately the transparent ITO electrode with thickness 200 nm treated at the same conditions. It can be observed transverse to the bending direction cracks. The results about ITO are in good agreement with existing reports, where similar effects have been studied [12]. In the reported results the minimum achievable radius of curvature for the ITO coated flexible substrate is 3-3.5 mm, because the produced films are thinner (50-100 nm), in comparison with our ITO film thickness (200 nm). We have already proved in our previous studies, that this is the optimum thickness for effective charge injection, low voltage drop and low interface capacitance, so this is the reason all experiments described here to be conducted at this thickness.

As can be seen in fig. 4, the sheet resistance abruptly increases with 35 % after increasing the number of bendings with one order of magnitude due to damages in the ITO electrode. After 2 000 cycles of repeating bendings sheet resistance has weaker sensitivity to the number of vibrations, because destruction of ITO has already been occurred at 2000 cycles. Although the graph is not shown, the trend in the sheet resistance change is the same with decrease of the radius of curvature during static bending from 5 to 2.5 mm (fig. 5), or it increases with almost 38 % after this test.

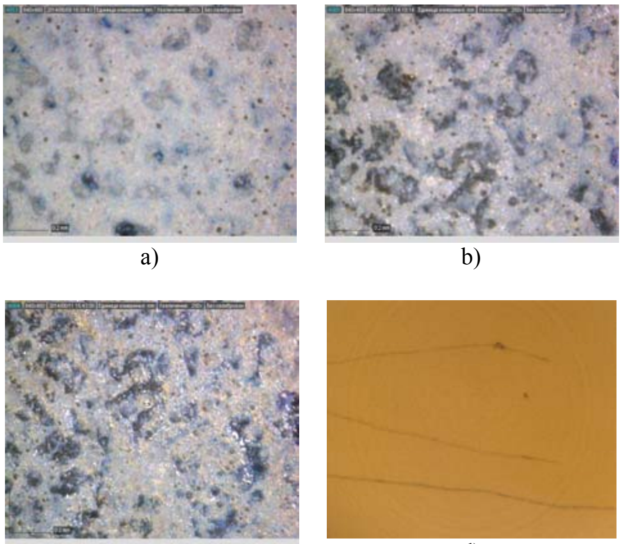

Fig. 3. Optical microscope images of the screen printed electroluminescent film: a) before bending; b) after bending at radius 5 mm for 1 hour; c) after bending at radius 2.5 mm for 1 hour; d) ITO 200 nm thin film cracked after bending at radius 5 mm for 1 hour.

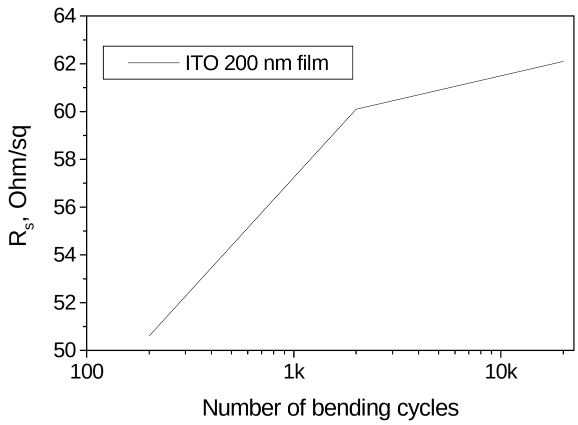

Fig. 4. Sheet resistance versus dynamic force applied on PET/ITO(200 nm) at 200, 2000 and 20 000 numbers of repeating bending.

Induced by bending internal stresses σ were determined based on the radius of curvature measurements, according to the following formula (Eq. 1) [13]:

$$\sigma = -\frac{E_s.h_s^2}{6(1-\upsilon_s)h_c}[1+\frac{h_c}{h_s}(4\frac{E_c}{E_s}-1)].(\frac{1}{r_2}-\frac{1}{r_1}) \quad (1)$$

where E_s and E_c are Young's modulus, respectively for the substrate and for the coating (it is product by the separated layers of ITO and electroluminescent ink, and the latter is product by modulus of all consisting components in the mixture); h_s and h_c are thicknesses of the substrate and coating (sum of the ITO and screen printed ink thickness); r_1 and r_2 are radii of curvature of the substrate and coating; υ_s is Poisson's ratio for the flexible substrate, that is average 0.4 for PET [14].

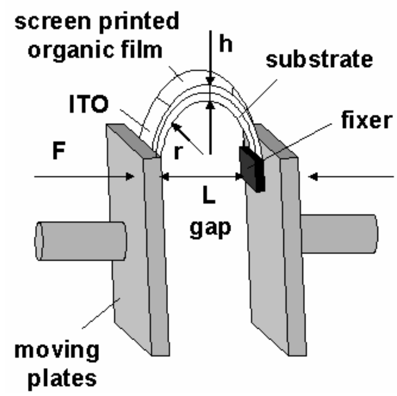

Fig. 5. Static stress supplied on structures PET/ITO/organic electroluminescent materials (later aluminum electrode is also added), causing different bending radius for 1 hour.

The data about the Young's modulus of the organic film, when it is deposited on PET substrates were taken from [15]. The negative sign in front the expression shows that the stress F is compressive. Fig. 5 shows the experiment in this case. Fig. 6 illustrates the calculated dependences between the internal stress and the radius of curvature for two different thicknesses of the organic electroluminescent layers.

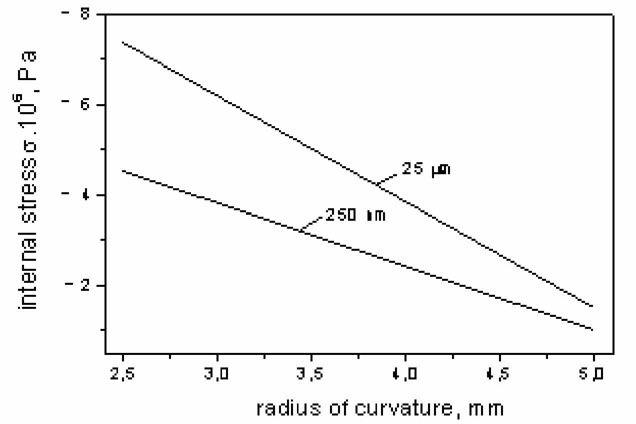

Fig. 6 Internal stress induced in organic electroluminescent films at different thicknesses as a function of the radius of curvature during bending.

The change in the mechanical state of the flexible OLED will result in the degree of recovering of the initial structure mechanically. It was found that the release of the induced strain does not lead to recovering of the sample initial electrical characteristics, or degradation of the device performance is irreversible. To estimate quantitatively this effect, we deposited aluminum electrode and measured the current-voltage (I-V) characteristics of the flexible OLED and compare them before and after bending at different radius of curvature (fig. 7). As can be seen the stability of the current flow at given voltage decreases with decrease of the radius of curvature. The maximum allowable current is restricted at voltages below 1 V after bending, because of the junctions' physical degradation. Although the graph is not shown, after dynamic test at 2000 repeating cycles of vibrations, the trend in the I-V curve is similar to that for static mechanical test at r = 5mm.

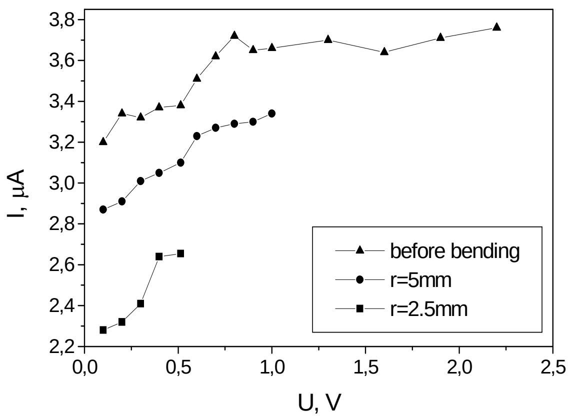

Fig. 7 Current – voltage characteristics of PET/ITO/screen printed organic layer/Al before and after static bending at radius 5mm and 2.5 mm.

IV. CONCLUSION

Organic layers are stable against strain due to the additional polystyrene binder introduced in the ink, but ITO film is brittle and degrades, causing degradation of the entire device. The results from the optical microscopy and current measurements show that the thick films are relatively durable at bending although the transparent electrode was not as durable as the organic ones. However, if the electrode film was more reliable, the flexible thick film electroluminescent devices would have longer lifetime. That's why our future work will be related to replacing this electrode by alternative conductive transparent film, having however higher elasticity and reliability to mechanical stress. Possible candidate is poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS).

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