

Investigation of the Defects Formation in Flexible Organic Light Emitting Devices by Thermal Activated Currents

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Abstract – Electrical behaviour of flexible light emitting devices at different temperatures was investigated. Organic electroluminescent layers were produced by different deposition methods – thermal evaporation in vacuum and spray coating. Thermally activated currents of the structures were measured in the range from 0 to 70 °C and the defect's origin, and activation energy were determined and compared for both cases. It was established that the thermal activated current for thermal evaporated films was higher (~900 nA) than for spray deposited (~430 nA) and consists of several distinctive peaks. Therefore higher defect density, embracing broad energy spectrum are typically revealed for the evaporation process and can be ascribed to structural films deformations. Just the opposite for the pulverization process there is only slight change in the current-temperature characteristic (~1nA/°C), which is evidence for lack of structural deep traps and presence of impurity defects or shallow traps.

Keywords – Organic light emitting devices, Thin films, Defects investigation, Thermal activated current.

I. INTRODUCTION

Organic materials used in light emitting devices serve as electroluminescent, hole transport or electron transport layers (HTL or ETL) [1,2]. These materials are either low molecular weight (small crystalline) or high molecular weight (polymeric) compounds [3]. Normally the first type is more widely spread, because of their higher quantum efficiency and they are deposited as thin films by thermal evaporation in vacuum [4]. For the needs of flexible organic light emitting displays (OLED), the high temperature deposition process must be replaced by lower temperature coating, like spin coating or spray deposition for example [5]. However, problems with the solubility in this class of organic semiconductors still exist, so mixture of different solvents have to be used for obtaining of homogenous solution and high quality films. Independently of the deposition method different varieties of defects are induced in the layers, like lattice imperfections, impurities or irregularities [6]. They affect on the charge carriers motion and prevent some of the main processes in the device like conduction and radiative recombination, therefore on the quantum efficiency. Defects concentration and energy distribution can be influenced and minimized by precise tuning of the deposition process and modes.

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Several techniques for defects parameters determinations are developed. Some of the more popular are thermally stimulated luminescence (TSL)[7], photo induced absorption (PIA) [8], etc. TSL is popular and usually applied method for luminescent materials, working on the emissive recombination principle, but in one OLED, there are HTL and ETL too. Another disadvantage is the difficulty in differentiation of electron traps and hole traps. This is the reason another quantitative measure to be chosen, like thermally activated current. Linear temperature activation (LTA) would cause simultaneously escaping of the whole entrapped charges without distinguishing of the specific energetic levels of the traps, releasing this charge. However, filling the traps at temperatures lower than the room temperature, followed by their controllable releasing with cycles of step increase of the applied thermal energy will lead to precise determination of the traps parameters.

In this paper modification of the method with thermally activation of charges (TAC) is developed and applied for investigation of defects in layers for flexible OLEDs. Low molecular weight compounds are deposited as thin films by vacuum thermal evaporation and spray deposition, and both layers are investigated for traps formation, defect density and energy distribution. It is proven that the spray deposited layers show lower thermally activated current and narrow spectrum of traps energies, which means that the pulverized structure is defect less and more favorable for high efficiently luminescent devices. By the author's knowledge this approach is still not applied for traps investigation in flexible OLED structures with sprayed layers.

II. METHODS AND MATERIALS

A. Theoretical Background of TAC Principle

By cooling the organic material to temperatures T_0 lower than the room temperature T_r , the charge carriers in the small molecules take place on the lowest unoccupied energy levels, which are their initial, stable states and there are no free charges in the gap even at supplied electrical field equal to the turn on voltage. At elevation of the temperature with a certain step of increasing charge carriers hop to the next unoccupied level and this moving can be detected by measuring of like very small current in the nano-ampere range. The current-temperature curve contains peaks, which mean activation and escape of charges at many different energy levels situated between the occupied and the unoccupied molecular levels of the organic molecules. These levels are traps for the useful charges and they are caused by structural defects formation or

introduction of impurities. They are energetically favorable states, so if the temperature is not further elevated the supplied electrical field would be not enough to cause charge releasing, so the conductivity in the device would be lower than the expected. If we can provide information about the density of states in the film and about their energy of activation we can optimize the deposition conditions in a way to minimize traps present. However, it must be taken into account that after heating of the material the relaxation time as a function of the temperature decreases and thermal motion of polarons is induced. It is responsible for the continuity of the current curves instead consisting of only discrete levels, corresponding to the traps activation energies. Fig. 1 illustrates the principle of thermally activated current measurement and its connection with the electrophysical properties of the organic layer.

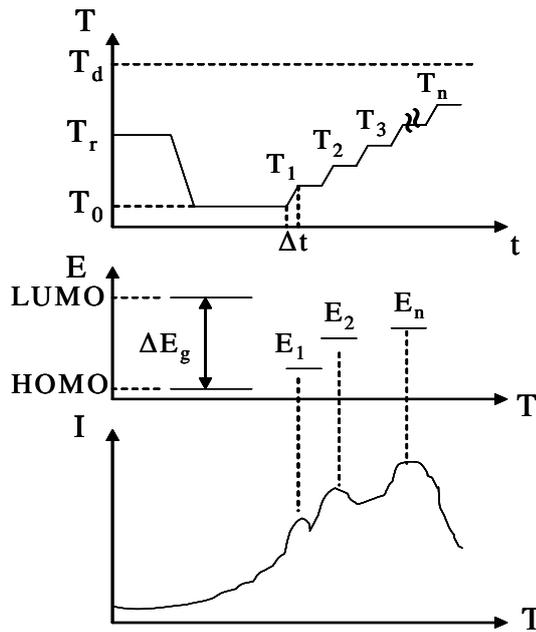


Fig. 1. Principle of thermally activated current measurement: T_d – temperature of organic material degradation or maximal temperature; T_1, \dots, T_n – temperatures, scanning the band gap for traps activation; HOMO – highest occupied molecular orbital; LUMO – lowest unoccupied molecular orbital; Δt – rate of temperature increase; ΔE_g – energy band gap of the organic semiconductor; E_1, \dots, E_n – energies of the induced traps, activated at temperatures from the range T_1, \dots, T_n .

Eq. (1) shows in general form the connection between the current, formed by thermally activation of the charge carriers, energy of activation of the traps and the applied temperature [9].

$$I(T) \approx \exp\left(-\frac{E}{kT}\right) \exp\left(-\frac{B}{\beta} \int_{T_0}^{T_d} \exp\left[-\frac{E}{kT}\right] dT\right) \quad (1)$$

where E is activation energy; T – temperature, k – Boltzman’s constant; B – heat capacity of the material; β – heating rate that the equipment can ensure; T_0 – initial low temperature. According to the initial rise method [10] the integral term in Eq. (1) is low for $T < T_{max}$ so the first exponent is predominant for the initial part of the TAC curve, where T_{max} is the

temperature where the current peak is situated. Then the current can be expressed only by the Arrhenius like equation. Activation energy can be determined by the rising slope of the current peaks (Eq.(2)).

$$E = \frac{kT_{max}}{\beta \Delta t} \quad (2)$$

B. Samples Preparation

On PET substrate, ITO film with thickness of 148 nm of was deposited by low-temperature reactive RF sputtering. The deposition conditions are oxygen partial pressure 2.10^{-4} Torr, total gas pressure in the vacuum chamber after sputtering gas (argon) bleeding is $2.5.10^{-2}$ Torr, sputtering power varies between 75 W and 105 W with rate 0.5 W/s during deposition of the initial ITO monolayer. Sheet resistance reaches 19.2 Ω /sq. after 10 minutes of ITO treatment with UV light (UV 365 nm, source power 250 W). The basic structure of the OLED devices is single layer, containing light emitting layer of tris(8-hydroxyquinolino)aluminium (Alq3; Sigma–Aldrich). It was situated between transparent ITO anode and nickel vacuum sputtered cathode. The organic dust was dissolved in solvent mixture from chloroform and methylethylketon heated to 40°C. Solution was stirred for several hours until fully dissolving was observed. For good adhesion of the Alq3 layer to the smooth surface of PET/ITO, additionally polymer polystyrene was added. For spraying, atomizer with nozzle having regulating orifice up to 200 μ m was used. The established optimal deposition conditions regarding layer uniformity was as follows: substrate temperature 70°C; distance nozzle-substrate 15 cm; pulverizing pressure 4 bars; solution concentration 5 mg/ml. Alternative structure with thermal evaporated Alq3. The thickness of the organic layer in both types of OLED structures is the same – 139 nm. The current was measured by a Keithley 6485 picoammeter with resolution 1 fA at special conditions, concerning electromagnetic guards and shields of the measurement circuit and thermal insulation of the chamber, where the Peltier element and the sample are situated. The temperature was measured by a temperature sensor with accuracy of 0.01°C.

III. RESULTS AND DISCUSSION

A. Technical Realization of the TAC Method

In A Peltier thermoelectric device is the main element in the specially designed apparatus for investigation of traps activation. This element works as cooler and heater, and switches over the two modes to reach temperatures in the interval 0–70°C. A block diagram of the setup is presented in Fig. 2. The heat is generated from pulse voltage, and it is transferred in portions to the sample with a narrow steps. The traps were filled after cooling the sample by applying forward turn-on voltage to the leads. The cooling cycle was followed by heating, and the shallowest filled traps determine the initial rise of the formed current flow. However, if the previous

heating to specific temperature has already released these shallow states, the initial rise in the next temperature interval will be conditioned by the traps from the next, deeper energy levels. The current value for each cooling-heating step was measured from the released charge carriers and consequently used for the trap concentration at certain energy. Peltier element PE-127-10-25 with maximum current 2 A was situated between two heat comb sinks for higher thermoconductivity. Additionally, the contacted surfaces were smeared with thermocontact paste to decrease thermal resistance. The heat sinks were enveloped with a thermoinsulating chamber, which closes a small bulk of air above the sample and thus eliminates heat (or cold)

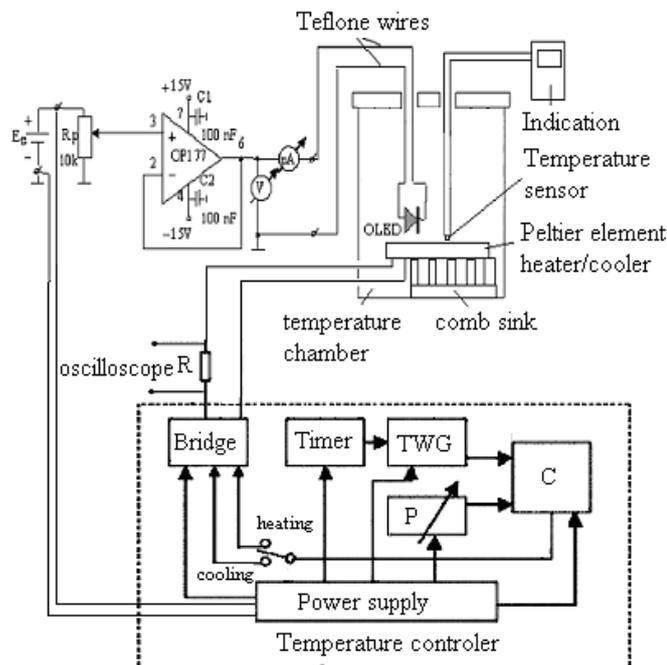


Fig. 2. Block diagram of the test circuit for thermally activated current measurement; TWG - triangle wave generator; P - potentiometer; C - comparator

dissipation into the surroundings.

The driving voltage was impulse and the rate of temperature change depends on its duty cycle, which is determined by a multi-turn potentiometer. The accuracy of establishment of the temperatures was 0.03°C , which allows scanning of energies in the band gap with resolution of μeV . Thus, precisely distinguishing even traps with close energy levels was possible. The rate of the temperature change was $2^{\circ}\text{C}/\text{min}$, providing abrupt heating/cooling and short time of the transient process.

Technically it is possible to be realized lower temperatures and steeper temperature fronts but it will cause condense from the big temperature difference and thermal stress. Besides, even at positive temperatures the conductivity abruptly decreases, because the organic materials are wideband gap semiconductors. It is not necessary faster temperature change, because the time for settle of the new state for the organic molecules is approximately comparable with the provided from this equipment.

B. Measured TAC for Thermal Evaporated and Spray Deposited Flexible OLED Structures

The samples, consisting of sprayed and thermal evaporated organic layers exhibit different thermal behavior, which can be detected by the TAC curves (Fig. 3).

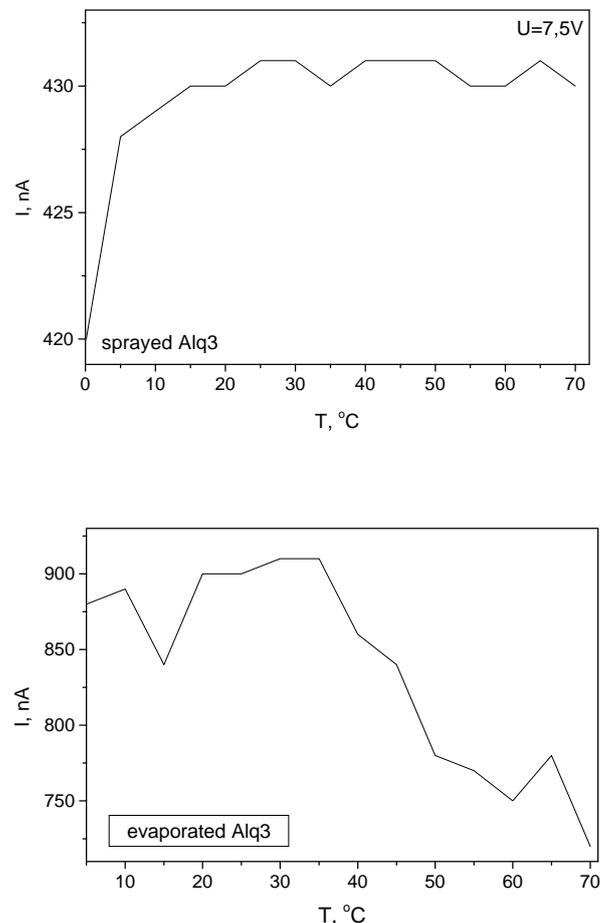


Fig. 3. TAC curves as a function of the applied temperature for spray deposited (up) and thermal evaporated (down) flexible OLED samples

For the thermal evaporated samples, the TAC is higher (~ 900 nA), which is indication for higher defect density, releasing bigger amount of charge carriers in the structure. The great numbers of abrupt peaks, closely situated in the curve are evidence for presence of defects having wide spread energies of activation. Their occurrence in the high temperature supplied range (above 42°C) shows "deep" traps formation lying close to the higher occupied molecular orbital or structural defects (not impurities). Based on previous observations [11] there is a reason to accept that the structural defects are caused by partially thermal degradation of the chemical bonds during thermal evaporation. The activation energies in this case are: 4.3 meV (10°C); 7.74 meV (18°C); 12.04 (28°C); 15.48 (36°C); 18.92 (44°C); 37.95 (65°C).

The relatively small TAC current for the pulverized layers (430 nA) is evidence for the low defect concentration and its almost permanent value at different temperature – for narrow

traps energy spectrum or four single (discrete) defect states. In this case, the origin of the defects can be ascribed as individual impurities incorporated in the layer, probably due to the lack of vacuum environment during pulverization. They cause “shallow traps” formation lying close to the lower unoccupied molecular orbital and easy activated even around room temperature (like for example at 16 °C and 27 °C). The activation energies of these discrete levels calculated according to the Eq. (2) are as follows: 6.88 meV (16 °C); 10.32 meV (24 °C); 17.63 meV (41 °C); 27.95 meV (65 °C). The dependences of the activation energy on the temperature for both technologies of organic films deposition are shown on fig. 4.

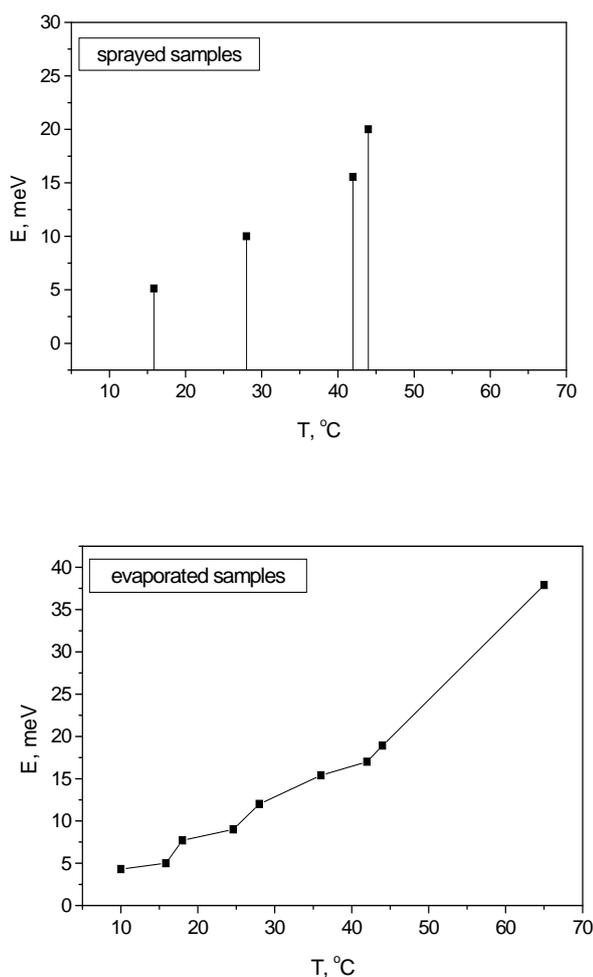


Fig. 4. Activation energy of the traps as a function of the applied temperature for spray deposited (up) and thermal evaporated (down) flexible OLED samples

IV. CONCLUSIONS

TAC is a very sensitive probe for internal organic structure investigation. Especially designed for the experiment home made equipment for supplying of heating and cooling in wide temperature range, allows scanning of the energy levels in the

organic semiconductor with μeV resolution. The current data illustrate that the spray technology is more suitable for deposition of organic layers in flexible OLED fabrication, because it is able to produce almost defect less structures. This leads to less captured charges, which can fluently contribute to the conduction process and light emission generation.

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