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Photodetector based on electrochemically deposited ZnO and inkjet printed PEDOT:PSS heterojunction

Nikolay Kurtev, Slavka Tzanova, Silvia Schintke

In this paper we present a new photo-sensible device based on ZnO/PEDOT:PSS heterojunction. The formation of ZnO layer was made by electrochemical deposition of Zn from zinc nitrate solution over a transparent ITO electrode on glass substrate. A precise thickness control of the Zn layer was performed by varying the current density during the deposition. A further open air thermal oxidation on hot plate was performed to convert the zinc to ZnO. In order to be structured the transparent conducting polymer PEDOT:PSS (poly(3,4-ethylenedioxythiophene) polystyrene sulfonate) was inkjet printed over the obtained ZnO layer. The current-voltage characteristic of the heterojunction was measured for daylight and dark modes. A Schottky barrier height as well as the ideality factor and series resistance has extracted using the forward current-voltage characteristics for both cases by using modified method for Schottky diode analysis.

Фотодетектор, базиран на хетеропреход от електрохимично отложен ZnO и принтиран PEDOT:PSS (Николай Куртев, Славка Цанова, Силвия Шинтке). *В тази статия е представен нов фоточувствителен прибор, базиран на хетеропреход ZnO/PEDOT:PSS. Формирането на слоя от ZnO е направено чрез електрохимично отлагане на цинк в разтвор на цинков нитрат върху прозрачен електрод индиево-калаен оксид върху стъклена подложка. С регулиране на плътността на тока по време на процеса е постигнат прецизен контрол върху дебелината на слоя. Превръщането на отложения цинк в цинков оксид е осъществено чрез термично окисление във въздушна среда. Структурирането на прозрачния проводящ полимер PEDOT:PSS (поли(3,4-етилендиокситиофен) полистирен сулфонат е осъществено чрез струйно принтиране върху получения слой от цинков оксид. Измерена е волт-амперната характеристика на хетеропрехода в два режима – на тъмно и на дневна светлина. Височината на Шотки бариерата, идеалзиращият фактор и последователното съпротивление на прехода са определени посредством модифициран метод за анализ на Шотки диоди, използвайки измерената волтамперна характеристика в двата режима.*

I. Introduction

The PEDOT:PSS is transparent organic polymer which is widely used for producing low cost, roll-to-roll and flexible electronic devices [1] such as OLEDs [2], flat panel devices, and sensors. Because of its optical transparency and high conducting properties it is suitable for light intensity sensors in which it forms a Schottky barrier (diode like) device with light depending current-voltage characteristics [3]. The conductivity of the PEDOT:PSS can vary in wide range (from 0.1 to more the 1000 S/cm) depending of the doping rate and other factors [4]. Typically the HOMO and LUMO levels are 5.2 and 3.5 eV respectively [5], [6], but they could also vary depending on the film treatment [7]. These properties makes the PEDOT:PSS attractive for transparent sensors applications using a Schottky barrier. Unlike the Schottky diodes made from silicon [8], [9] the direct formation of a Schottky barrier between the PEDOT:PSS and the most used metals in microelectronics (copper, aluminium, gold, silver etc.) is not possible because of the closely situated energy levels (it forms an ohmic contacts). For this reason a second active layer must be applied in order to make a sufficient energy barrier.

In this paper we present our study of photo sensible device that uses as active layers inkjet printed PEDOT:PSS and electrochemically deposited zinc followed by a thermal oxidation to ZnO. The external electrodes are formed by high conducting (8-12 Ω/sq.) transparent ITO for the ZnO side and Ag (obtained from the silver paste) for the PEDOT:PSS side, which provides the ohmic contacts (linear I-V characteristics) with the active layers.

The Zinc oxide (ZnO) is a semiconductor (n-type) with large bandgap (3.3 eV) and large exciton binding energy (60 MeV) [6], [10]. During last years it has been largely studied [11]-[14]. The formation of ZnO thin films is relatively easy by several methods mainly by sol-gel processing [15], [16], by solution growth [17] but also by inkjet printing [18] or indirectly (by high temperature annealing) from pre-deposited zinc [19]. The last method was used in our work because of its simplicity and possibility to control of thickness of Zn (ZnO) precisely by varying the current and/or the time of the electrodeposition.

II. Background

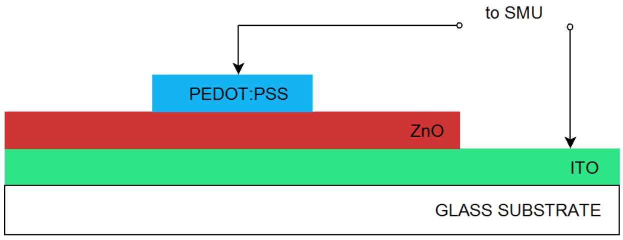
The photosensible ZnO/PEDOT:PSS devices are investigated recently. In [3] a UV photodetector based on ZnO/PEDOT:PSS junction was characterized, using two different methods to extract the electrical parameters. A study of the I-V characteristics and energy level diagrams of the PEDOT:PSS and ZnO is made in [6]. However we have developed a ZnO/PEDOT:PSS heterojunction using inkjet printing and electrolyze deposition methods. The here proposed combination is suitable also for flexible substrates as PET or PEN as well as for transparent applications

The fabricated light sensitive device structure ZnO/PEDOT:PSS has been furtherly investigated by measuring the current-voltage curves in daylight and dark conditions. From the obtained curves a device parameters such as Schottky barrier height ϕ_B, ideality factor n, and series resistance R_s were extracted by a modified Cheung's method [20], [21] using the logarithmic plots.

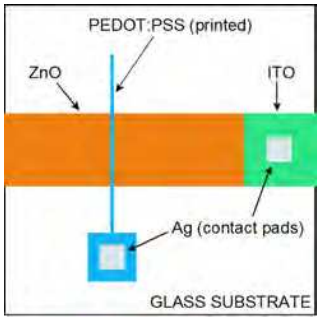
III. Sample preparation

The structure of the investigated photo sensible device is shown on Fig.1. It was obtained on a glass substrate. An ITO electrode was patterned by chemical etching with hydrochloric acid on ITO covered glass substrate (25 mm x 25 mm), purchased from Sigma Aldrich (R = 8-12 Ω/sq). The width of the electrode is (5 ± 0.1) mm and the length is 25 mm. The formation of ZnO layer has been made in two stages: (i) electrodeposition of pure Zn from zinc acetate solution and (ii) thermal oxidation of Zn on ambient air to ZnO.Different sections of the text must be formatted as described below.

For the electrodeposition of the Zn an electrolyte solution has been prepared in beaker by dissolution of 1.5 g zinc acetate hexahydrate ($N_2O_6Zn.6H_2O$, Sigma Aldrich, 297.49 g/mol) into 100 ml deionized water at room temperature with electromagnetic agitation for 10 min. The patterned ITO structure was used as negative electrode which has been immersed 18 mm into electrolyte solution. The positive electrode was made from thick aluminium foil with approximately the same surface as the ITO electrode. The distance between the electrodes is 25 mm and the supply voltage is 2.1V. On Fig. 2 the deposition current is presented over the time. The decrease of the current is explained by the saturation of the surface with the Zn^+ ions. After the zinc deposition the sample was rinsed in deionized water and was dried by N_2.



(a)



(b)

Fig.1. Photo sensible device composed by PEDOT:PSS and ZnO active layers. Electrodes made from ITO and Ag. (a) Cross section overview with electrical contacts for source measurement unit (SMU) to provide current-voltage characterization (b) Top view of the structure.

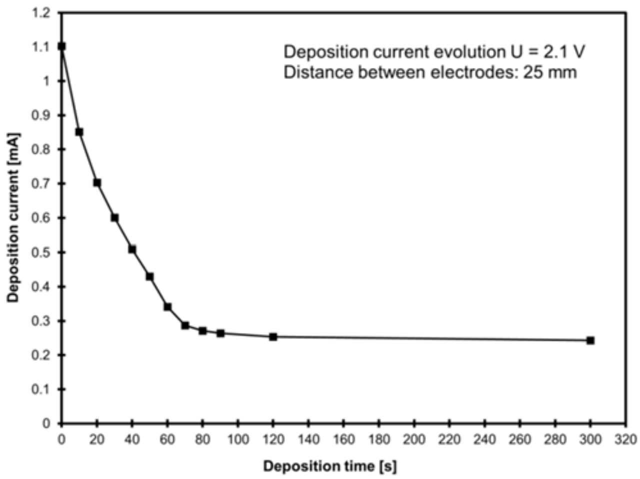


Fig.2. Current evolution during the Zn deposition procedure.

Thermal annealing on a hot plate is used to transform the Zn layer to ZnO. In order to avoid mechanical cracking of the film and glass substrate the sample is gradually heated from room temperature to 555°C during 15min using steps of 30-40°C, followed by a 45 min annealing at the final temperature. After the annealing process the sample is left on the hot plate (cooling down) until reaching of the room temperature.

After the formation of the ZnO/ITO structure the sample rinsed in deionized water for 1 min and dried with nitrogen. In order to form the device junction, a PEDOT:PSS wire was inkjet printed perpendicularly over the ZnO/ITO electrode (Fig. 1b). PEDOT:PSS conductive ink was purchased from Sigma Aldrich and a microplotter from SonoPlot was used. The resulting contact area PEDOT:PSS and ZnO is S=1.065 mm^2, as determined by optical microscopy and image analysis with ImageJ software [22].

For electrical probing, contact pads on PEDOT:PSS and on ITO are made with silver paste (Fig 1b) with further drying at 90°C for 5 min. The electrical characterization is performed using electrical microbot probing system (miBotTM, Imina Technologies) and a Keithley 2401 source meter controlled by LabVIEW software.

IV. Results and discussion

Fig. 3 shows a measured current voltage characteristics for negative and positive bias in two different modes: daylight and dark. The forward and the backward currents are bigger for daylight mode which can be explained with the increased mobility of the carriers due the photon excitation. The I-V characteristics have diode behavior, which is proven by a smaller backward current in comparison with the forward. The difference between the obtained I-V curve and the theoretical model [25] can be explained by the porosity of ZnO films [23] or by the polycrystalline nature of ZnO and possible defects in ZnO/PEDOT:PSS interface as well as low carriers mobility [6]. Although, the high value obtained for the ideality factor (discussed further) is confirmed for those types of devices [6], [24].

A good theory concerning Schottky barrier height can be found in [25]. From the theory the forward current for a Schottky junction is given by the thermionic emission model. For our device we need to add also a series resistance to a junction in order to model the volume resistances of the PEDOT:PSS and ZnO which are not negligible. We have used the equation for thermionic emission into this form:

$$I = I_s\left[exp\left(\frac{q(U - IR_s)}{nkT}\right) - 1\right] \quad (1)$$

where I_s is the saturation current (the equation can be found in [21]), q the electron charge, U the applied voltage to the contact pads, I the current thought the device, R_s the equivalent series resistance, n the ideality factor, k the Boltzmann constant, and T the temperature in K.

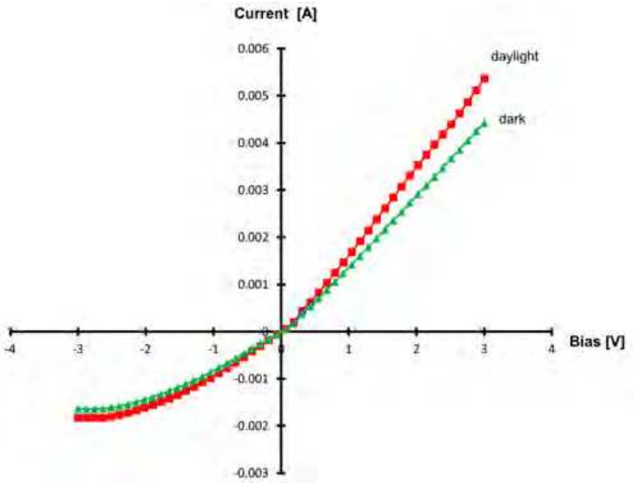


Fig.3. Current-voltage characteristics for positive and negative device bias in daylight and dark conditions.

In order to extract the device parameters such as Schottky barrier height ϕ_B, the ideality factor n and the series resistance R_s we apply a modified Cheung's method [20]. The semi-log plot of the forward device current density is shown on Fig. 4.

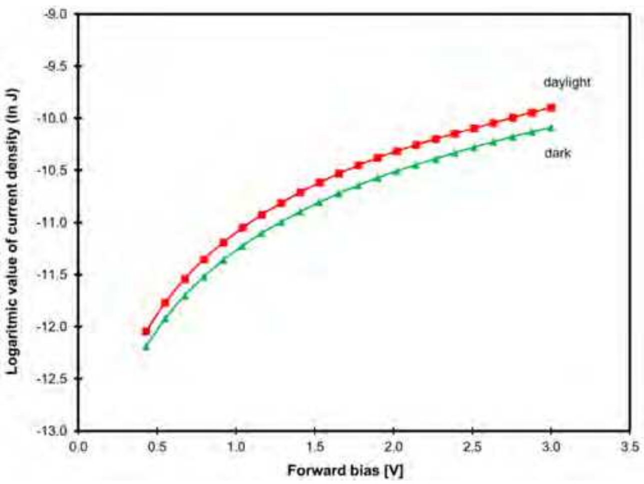


Fig.4. Semi-log forward current density plots for daylight and dark mode.

According to the method, on Fig. 5 we express the dU/d(ln J) in function of the current density for the two modes – daylight and dark and also a H(J) plot in order to determine the device parameters by equations (2) and (3):

(2) $$\frac{dU}{d(\ln J)} = R_s SJ + \frac{n}{\beta}, \quad \text{where } \beta = \frac{q}{kT}$$

(3) $$\frac{dU}{d(\ln J)} = R_s SJ + \frac{n}{\beta},$$
$$\text{where } \beta = \frac{q}{kT} H(J) = R_s SJ + n\phi_B$$

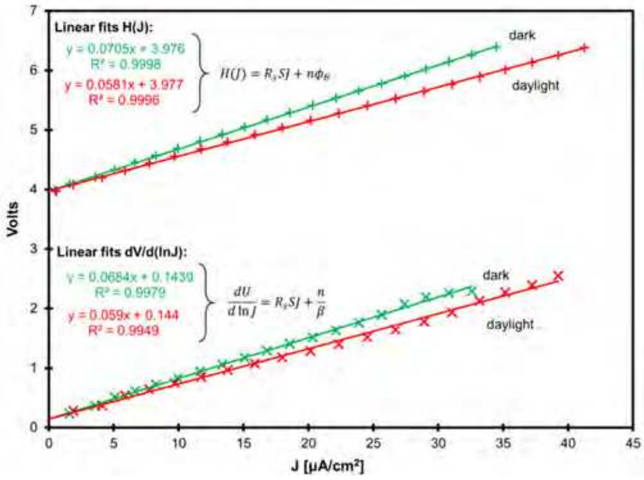


Fig.5. Linear fits for the dU/d(lnJ) and H(J) functions.

Using (2) and (3) from the given linear fits we calculated the Schottky barrier height, the ideality factor of the junction. The equivalent series resistance is calculated from both equations with roughly 3% difference. This was used as secondary verification of the results. Tabl. 1 shows the calculated values with corresponding errors for daylight and dark mode of the photodetector.

Table 1

Extracted values for the Schottky brier height, ideality factor and equivalent series resistance for photodetector.

	ϕ_B [eV]	n	R_s [Ω] from (2)	R_s [Ω] from (3)
daylight	0.71 ± 0.02	5.6 ± 0.1	590 ± 15	581 ± 3
dark	0.71 ± 0.02	5.6 ± 0.1	684 ± 11	705 ± 4

The values obtained from the Schottky barrier height are close to other similar devices [6], [24]. The fact that the barrier is practically the same value for the two modes (dark and daylight) and also the values for the equivalent series resistance obtained from (2) and (3) shows the fidelity of the used method.

The ideality factor is introduced to express the imperfection of the current-voltage characteristic from the ideal diode curve. For an ideal diode it must be equal to 1. As the investigated characteristic is more different from the ideal, the ideality factor has higher value. For the heterojunction ZnO/PEOT:PSS the obtained value of the n is confirmed by other works [6], [24]. This is due the porous and polycrystalline structure of the ZnO thin films which creates multiply current pathways [6]. We suppose that the ideality factor may be improved using different conditions or technology for ZnO layer deposition [26], [27].

The series resistance is also in the expected ranges. We can suppose that the polymer region of the junction has almost the whole part of this series resistance. In a previous work we have found that the sheet resistance for this type of the PEDOT:PSS ink is about 695 Ω/sq that means that the performance of the device may be improved if a more conductive ink is used.

V. Conclusions

In this work we have made and characterized a photodetector based on ZnO/PEDOT:PSS heterojunction. For the formation of the ZnO thin layer we have used an electrodeposition of Zn and thermal annealing. The PEDOT:PSS was inkjet printed on the obtained ZnO thin film.

The device was electrically characterized by measuring the current-voltage characteristic for positive and negative biases and device parameters like Schottky barrier height, ideality factor and equivalent series resistance were extracted using the function slopes.

The values found were confirmed for the two experimental setups (for daylight and dark modes) and also for two different equations. We have estimated that the Series resistance of the junction is more situated into the polymer side of the junction and we plan like future work to make an optimization of this device.

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