

Creation of a Tunable Diode Based on Nanotubes with an Ion Gate

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The new concept of an electronic tunable device based on nanostructured materials is suggested. A tunable organic diode is represented by the example of a vertical architecture with a polymer layer of poly-3 hexylthiophene-P3HT and an upper carbon electrode whose properties vary in a wide range when it is doped in a double electric layer in an ionic liquid. Two types of ionic liquids with different ion sizes and different breakdown voltages are used. It is shown that diode based on nanotubes plus organic can be used for photodetectors and in photovoltaic elements

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1. INTRODUCTION

The diode, like an electronic solid-state device with two electrodes was created at the silicon microelectronics start. It is historically the first useful semiconductor device, a current rectifier. During the work, the solid-state diode is opposed to an organic diode, since there are a number of distinctive features in their work principles. Detecting what they differ from each other, and in what their functional properties are similar, it will be possible better to explain and understand how the tunable organic diode works. Rectifiers work using the asymmetry principle. If the vacuum diode operates based on the cathode and the anode asymmetry principle, where the cathode emits electrons, and the anode with the + sign receives them, then work in the opposite direction is impossible. Solid-state inorganic diodes work using the doping asymmetry. If doped *n*- or *p*-regions are created in an inorganic semiconductor, carriers depletion and an internal electric field equal to the contact potential difference appear at the contact site of the regions. This field, with a sufficiently high intensity, spreads over several microns, and allows separating charges of different signs (+ or -), so that when a positive bias is applied to the *p*-region and negative one to *n*-region, the electric field is rectified and electrons can move along the horizontally at conduction band bottom, and holes move along the valence band, respectively. When the reverse voltage is applied to *p*- and to *n*-regions, the energy of the conduction band level rises, the level of the valence band descends, hence the electric field amplifies, the depletion zone expands and charges that move to the electrodes cannot overcome this energy barrier. In this case the circuit current is called the saturation current of the back branch, it is the current of the minority charge carriers moving through the field.

2. RESULTS AND DISCUSSION

One of the main diode characteristics as device is the rectification coefficient, which is equal to the ratio

of the current at a certain voltage on the straight line and the reverse branch of the *I-V* characteristic $-K = I^+ / I^-$.

For standard inorganic diodes, the rectification coefficient reaches values from 10^3 to 10^8 . Inorganic diodes, devices with doped areas, are low-impedance devices having basic charge carriers with initial concentrations of the order of 10^{16} - 10^{20} cm³.

In turn, an organic asymmetric diode is characterized by the fact that an organic semiconductor, for example, a poly-conjugated polymer, poly-3-hexyl thiophene, is placed between two electrode plates, indium tin oxide and aluminum respectively [1-5].

In this case, the asymmetry is set by the electrodes, the difference in the output work functions. One electrode has a large work function F_1 , the other has a small F_2 , thereby creating an embedded field. This is due to the fact that in a closed system the level should be at a single level, and when the leveling occurs without any displacement, the slope of the zones appears. That is, from ITO to aluminum, the slope of the zones appears, which corresponds to the appearance of an electric field linearly distributed throughout the organic semiconductor depth.

This happens due to the polymer does not have the main charge carriers, the corresponding device is high-resistance, there are no charges that could screen the field as in the inorganic *p-n* junction, so the field in the organic diode is evenly distributed. The aluminum electrode is supplied by negative voltage ITO is positive, while the aluminum level is shifted up, ITO is shifted down. Next, the potential is equalized, the electric field in the film depth becomes zero, hence the charge carriers can move freely as the external displacement increases, which corresponds to the direct branch of the *I-V* characteristic.

At reverse bias on the reverse branch (positive bias is applied to the aluminum electrode, ITO is negative). The level of ITO rises still up, aluminum is still down, so the built-in field increases even more, so when holes are injected from the ITO to the valence band, they need to move against the electric field, that is impossible, so the

regime becomes locking (similarly with the electrons injecting from the conductivity band and their motion along the field). Thus, a very low current and large rectification coefficient appear. If a large displacement is applied to a straight branch, then an inverse electric field arises that helps electrons to move against the field and holes move along the field. Summarizing the features of the organic diode, the following important details can be distinguished. First, asymmetry arises due to the difference in electrons work output, it forms an embedded electric field uniformly, and linearly distributed over the polymer depth, undoped layer. Second, the electrons and holes injection arises from overcoming the potential barrier, the holes injection from the ITO occurs with a smaller potential barrier overcoming than when electrons are injected from aluminum. By influence on two parameters, the output level and injection, it becomes possible to control the properties of the diode. In turn, the control of these properties in nanostructured materials occurs in a wide range due to their unique properties.

The device consists of two parts connected in parallel to each other. The first part consists of two electrodes with a P3HT polyconjugated polymer between them, the design assumes a glass substrate ITO layer as an anode, a P3HT layer of 200 nm, and carbon nanotubes deposited by lamination. The second - the diode design is a layer of ionic liquid, DEME-BF₄, enclosed between two electrodes made of carbon nanotubes, this part of the device can be called as a capacitor or supercapacitor. Thus, a capacitor connected via a common electrode (carbon nanotube) and a diode. The levels location of the ITO, P3HT, carbon nanotubes is shown to the left, where the nanotube levels are located at a distance Δ_2 from the bottom of the valence band, ITO at a distance Δ_1 , which are so-called barriers for hole injection, these barriers are small enough. This arrangement is obtained as a result of not too big a difference in the work function of the ITO and nanotubes - 4.9-5.3 eV, which are close in value to the P3HT valence band bottom 5.3 eV. Then there are two energy levels of carbon nanotubes, they lie in one position, since there is no bias between them, which will be the voltage at the gate (U_{gate}). The voltage between the ITO and nanotubes is denoted by the $U_{source-drain}$ voltage.

The device working regimes: $U_{gate} = 0$

When the gate and drain-source voltage is 0, the Fermi level in the system is one, then we have a horizontal arrangement or a very small slope, which forms an insignificant electric field.

$U_{gate} > 0$. If negative bias is applied to carbon nanotubes, and positive to ITO, then the operation mode will be formed in the forward the I-V characteristic branch. Holes will be injected through the barrier into the valence band of the polymer, they will start moving up the field, its form will be a straight line similar to the I-V characteristic of the resistor, or have a slight slope caused by injection into the barrier.

$U_{gate} < 0$. At the reverse bias, a symmetric process occurs, forming the inverse branch of the I-V characteristic.

When the ion part of the super-capacitor is turned off, the device operates as a resistor, there is no current

rectification, $K = 1$. The effects that arise when the supercapacitor is switched on will be shown more clearly by the example of the experimental data obtained. The following processes and materials were used to create the organic diode.

- 1) ITO substrate, pixel width - 2.8 mm;
- 2) The carbon nanotubes strip width is 5 mm;
- 3) The pixel area is 0.14 cm²;
- 4) Polymer semiconductor layer – P3HT, spincoating of the solution at a 25 mg/ml concentration in chlorobenzene at a 1000 RPM rate (60 s), annealing 100 °C (40 min).
- 5) Coating, sealing carbon nanotubes by HFE, drying at 80 °C, distance between electrodes of nanotubes is 2 mm.
- 6) Supply of silver contacts, wires, installation in the tooling for measurements.
- 7) Formation of a liquid layer of DEME-BF₄ ionic liquid – 100 μm under a cover glass.
- 8) Gate voltage 0 U_{gate} minus – U_{gate} plus,
- 9) Measurement of the I-V characteristics of the Source 2 – Drain 2 diode;
- 10) Measurements of the nanotubes bound resistance Source 1 – Drain 1;
- 11) The applied biases are 0; 0.5; 1; 1.5.

With the supercapacitor turned off, the device behaved like a resistor. A slight slope, as it was supposed to be formed by injection into a barrier.

Further, when the supercapacitor is turned on and the corresponding voltage is applied to the gate, the I-V slope began to change, gradually assuming the form of the current-voltage characteristic of the diode (Fig. 1).

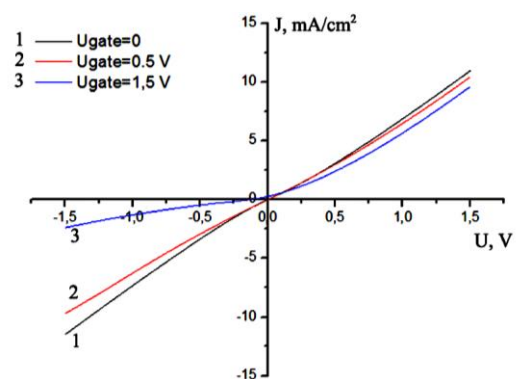


Fig. 1 – I-V characteristic for a diode with the corresponding applied voltages to the gate: 0; 0.5; 1.5

This changing process the operating mode of the current-voltage characteristic is due to the carbon electrodes charging by ions from the ionic liquid, with a positive bias applied to the counter electrode and negative bias to the working electrode. The positive ions come to the working electrode under the drift influence that, in addition to penetrating into the 3D nanotubes net structure, diffuse between the polymer chains, respectively doping it, enriching the minority carriers, and forming a p-layer, which in turn creates a p-n junction (Fig. 2). As the displacement on the gate increases, the region gradually grows.

Also, the doping process was seen visually, the P3HT polymer began to change its color, with a gate voltage of 1, 5 V.

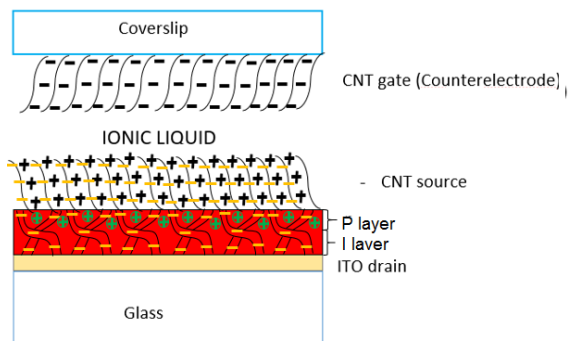


Fig. 2 – Diagram of polymer doping at charging mode

Measurements of the carbon nanotubes resistance at the supercapacitor disabled also showed the characteristic of the resistor (Fig. 3).

However, an increase in displacement at the gate also indicates the carbon nanotubes charging themselves when collecting ions of opposite sign, as a result, the nanotubes *I-V* has a small slope and shows the performance of the electrochemical cell, as shown in Figure 4, this process was accompanied by a significant decrease in the resistance of carbon nanotubes (Fig. 5).

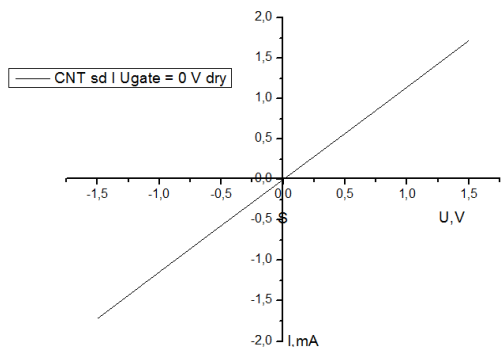


Fig. 3 – *I-V* for carbon nanotubes with a supercapacitor disconnected and no external displacement

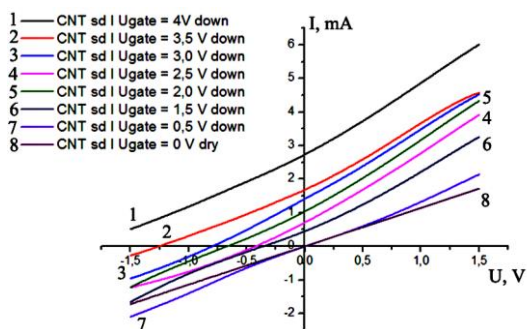


Fig. 4 – *I-V* for carbon nanotubes layer with an external bias applied to the gate and ion charge

Directly, the charging rate and, correspondingly, the rate of doping characterize the charging current between the working and counter electrode of the nanotubes. At low voltages, the charging current was characterized by a microampere level and a slow drop with a saturation output (Fig. 6), which means the charging process end, but at a voltage of 1.5 V there was a high increase in the charging current with a saturation output only in the milliamper range (Fig. 7-8).

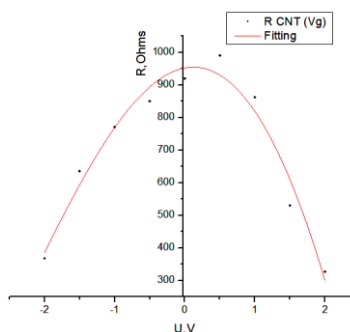


Fig. 5 – The carbon nanotubes resistance vs the voltage on the gate

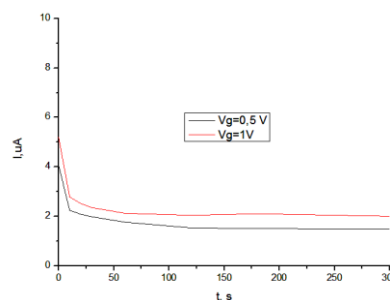


Fig. 6 – Charging current at low gate bias voltages

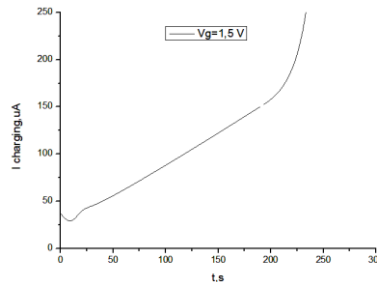


Fig. 7 – Charging current at a bias voltage at the gate 1.5V

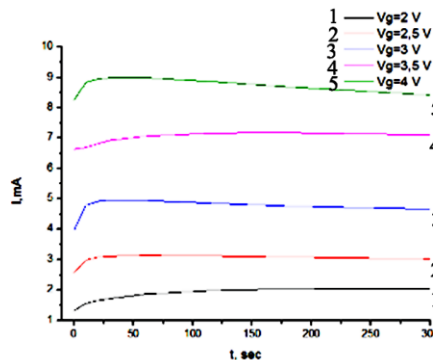


Fig. 8 – Charging current for a large bias voltage at the gate more than 1.5V

3. SUMMARY

During the work it was shown that without the appropriate nanotube electrode charging, the device organic polymer-nanotubes bound structure behaves like a resistor with a linear form of the *I-V* characteristic. However, when the nanotubes are ionically charged by n-type, the asymmetric diode properties with a high dependence of the rectification factor on the nanotubes

charging voltage and on the ionic liquid type are detected. The result of the work shows that this type of asymmetric organic diodes can be used both for organic photodetectors and for photovoltaic cells.

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