Electrical Properties of Organic Semiconductor Orange Nitrogen Dye Thin Films Deposited from Solution at High Gravity

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Abstract

In this study the electrical properties of organic semiconductor orange nitrogen dye (OND) have been examined. Thin film samples were deposited from OND solution in water on a nickel substrate (it was the first electrode) at room temperature at different gravity conditions including, 1 g (reference samples), 123 g, 277 g and 1107 g by a centrifugal machine. As a second electrode of the samples a gallium drop was used.

The voltage-current characteristics of the samples were measured at temperature interval of 30°C – 60°C. It was found that all voltage-current characteristics were asymmetrical with slightly rectification behavior. The resistances of the samples decrease monotonously with temperature but with acceleration they show minimum around of 123 g. As a rule the forward bias resistance ("+" voltage was applied to gallium) were less than reverse bias ones ("+" voltage was applied to nickel).

The electric behavior of the samples analyzed by the conception of space-charge limited currents (SCLC) at the presence of two different kinds of metallic electrodes (Ni and Ga) in the samples.

Introduction

The organic semiconductors may be found suitable for application in many fields of electronics depending of their response to electrical conductivity [1,2] and very often it determines the characteristics of the devices. For example, the efficiency of organic solar cells is generally limited due to the low conductivity of photosensitive materials [3,4]. This investigation deals with organic semiconductor such as orange nitrogen dye (OND) that has the potential for applications in electronic engineering. It is known that the structure and properties of organic semiconductors highly depends upon their processing technology [1,2]. Generally, the organic materials have large molecular weight, strong intramolecular and weak Van der Waal's intermolecular bonding. For this reason organic materials and particularly semiconductors are found suitable for centrifugal processing that has given interesting results [5-7]. The poly-N-epoxipropylcarbazole films grown from solution during rapid stirring [5] showed higher conductivity than that of the reference samples. In [6] it was investigated the electrical conductivity of films composed of two photosensitive organic semiconductors poly-N-epoxipropylcarbazole and copper phthalocyanine deposited from solution at different gravity conditions from 1 g to 1107 g. It was found 1.5 – fold increase in the conductivity and 2-fold decrease of activation energy with increased acceleration. Deposition of copper phthalocyanine organic thin films in high gravity by physical vapor transport was studied in [7]. It was shown that the optical absorption increased with increasing acceleration during film growth. Moreover, the peaks shifted to lower wavelengths values as the acceleration was increased. X-ray diffraction indicated that the centrifugal force caused the crystals constituting the films to be strained.

Last time Schottky-barrier, in particular, organic-metal junctions were investigated widely [8-10], because fabrication of their is simple, inexpensive and may be promising especially for different kind of sensors for electronic devices. In [8] it was investigated metal free or zinc phthalocyanine with ohmic

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contact (Au) and a blocking contact (Al or In) and it was observed strong rectification and photovoltaic effects. The photovoltaic properties of Au/polyvinylcarbazole – trinitrofluorenone complex/Al cells were examined in [9]. Here polymer thin films were formed by the solution-casting method. In [10] it was studied three kinds of phthalocyanine (Pc) thin film solar cells, *i.e.* ITO/Pc/Al, ITO/Pc/In and Al/Pc/Au. All the Pc thin films were deposited by vacuum evaporation. The cells showed rectification and photovoltaic effects in the visible wavelength region.

Electric properties of some organic films deposited at high gravity was analyzed by the conception of space-charge limited currents (SCLC) [11] that may find some applications in practice as varistors: the poly-N-epoxipropylcarbazole-copper phthalocyanine films showed highly non-linear voltage-current characteristics. For practical utilization of semi conductive organic thin films it would be important to investigate their electrical properties with different metals (as electrodes) in order to identify where they form ohmic contact or Schottky type barrier. In this paper we present the results of investigations of electric properties by measurement of voltage-current characteristics of OND thin films deposited from solution at high gravity conditions by centrifugation.

Experimental

In this work commercially produced OND ($C_{17}H_{17}N_5O_2$) was used. Figure 1 shows the molecular structure of the OND. Molecular weight of OND was 323 g/mole. Thin film samples were deposited from 5 wt.% solution of OND in distilled water at room temperature at different gravity conditions including, 1 g (reference sample), 123 g, 277 g and 1107 g by a centrifugal machine (g is gravitational acceleration).

A tabletop centrifugal machine [6] was used for the deposition of films on the 15 mm diameter nickel substrate (0.1-0.2 mm thick). The substrate was placed inside an aluminum vessel, which was mounted in the centrifugal machine. The centrifuge had an 11 cm arms and could provide acceleration up to 1107 g at its maximum rotation speed of 3000 rpm. For every experiment two symmetrically installed aluminum vessels filled by solution of equal volume (0.5-0.7 ml) were used.

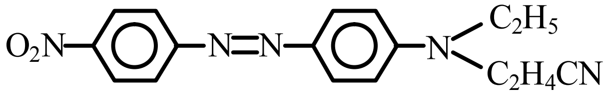

Fig. 1. Molecular structure of orange nitrogen dye (OND).

The solution was evaporated due to high gravity at room temperature and atmospheric pressure without any additional heating. At the acceleration of 123 g, 277 g and 1107 g the processing time of 30-50 minutes, 20-30 minutes and 10-20 minutes, respectively was sufficient to evaporate the solvent completely and to deposit the films. Reference samples were deposited at 1 g and took more time to evaporate completely. Visual inspection showed that the red color of OND was evenly distributed at high gravity implying more homogenous films as compared to the film deposited at 1 g.

Ni substrate served as first electrode while a droplet of liquid gallium (at room temperature) was a second electrode, diameter of it was equal 3 mm, so the structure of samples was Ga-OND-Ni. In some experiments as a first and a second electrodes two gallium drops were used, *i.e.* the sample had in this case the following structure: Ga-OND-Ga. The thickness of the films was determined by the measuring of weight of the deposited matter with density of OND taken as 0.9 g/cm^3 [12]. It was also estimated by scanning electron microscopy. The thickness was in the range of 0.5 μm (deposited at 1107 g) to 5 μm (deposited at 1 g). It was observed that the thickness of the films decreases with the increasing acceleration. It may also be pointed out that the thickness is calculated assuming a constant density, however, the density of materials may increase at high gravity. Therefore, the estimated thickness from weight measurements may give larger than true values.

Measurements of Voltage-Ampere characteristics were carried out by using of conventional digital voltmeter and ammeter at the temperature interval of 30°C – 60°C, temperature was measured with error ± 0.5%.

Results and Discussion

Figures 2 and 3 shows, as examples, the voltage-current (V-C) characteristics of the OND films deposited at 1g (reference samples) and 123 g respectively at 30°C and 60°C: polarity of the voltage shows potential applied to the gallium electrode. It is seen that characteristics are quasi-linear with slightly rectification behavior: forward bias is observed at positive potential applied to gallium and reverse one – at positive potential applied to nickel electrode. This figures show that currents increase with temperature as well.

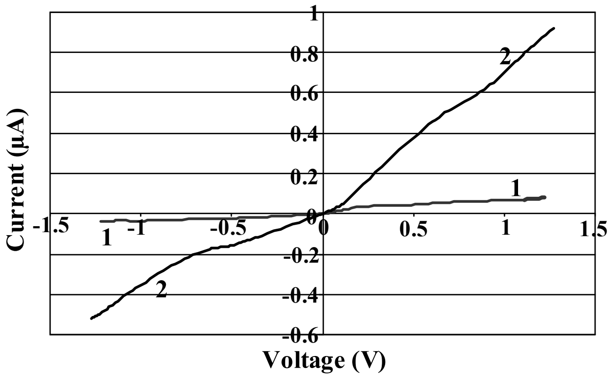

Fig. 2. Voltage-current characteristics of OND film deposited from solution at 1 g (reference sample), measured at: 1- 30°C, 2- 60°C.

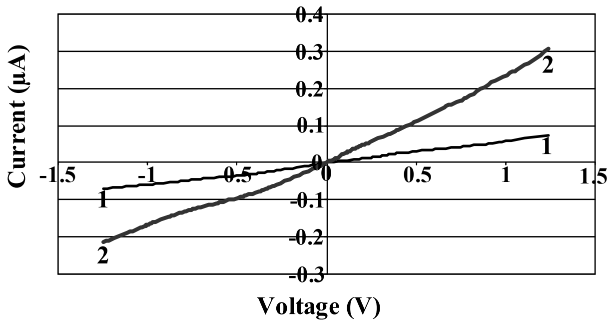

Fig. 3. Voltage-current characteristics of OND film deposited from solution at 123 g, measured at: 1- 30°C, 2- 60°C.

From voltage-current characteristics forward bias (R_+) and reverse bias (R_-) resistances of the samples were determined as ratio of voltage and current increments at positive and negative polarities of applied voltages respectively. Figures 4 and 5 show dependences of R_+ and R_- on temperature for samples deposited at 1 g and 123 g respectively. It is seen that $R_+ < R_-$ and both quantities decrease monotonously with temperature. The resistances R_+ and R_- for samples deposited at 123 g are less than for the ones deposited at 1 g. The averaged room temperature conductivity of samples deposited at 1 g was equal to 2.4×10^{-10} $ohm^{-1}cm^{-1}$.

Figure 6 shows dependences of R_+ and R_- on acceleration (a) at room temperature (T=30°C). It is seen that the dependences have minimum around of 123 g – 277 g. This result has practical importance: any decrease of the resistance of the organic semiconductor films obtained by some technological modification decreases internal resistance of the semiconductor devices made from this material and finally increase in the efficiency of the one, for example, solar cells. On the other hand the decrease in R_+ and R_- is not monotonous and obviously there is optimal accelerations: in this case in the interval of

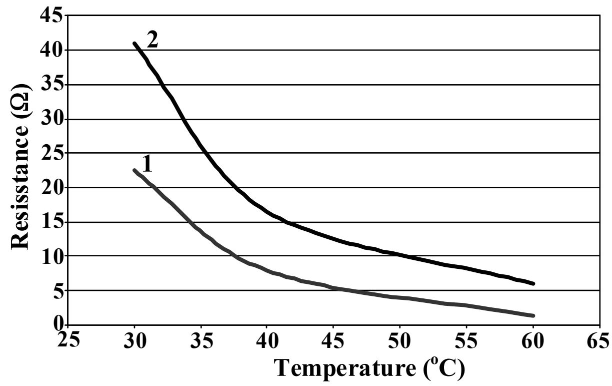

Fig. 4. Dependences of forward bias R_+ (1) and reverse bias R_- (2) resistances of the OND film deposited at 1 g on temperature.

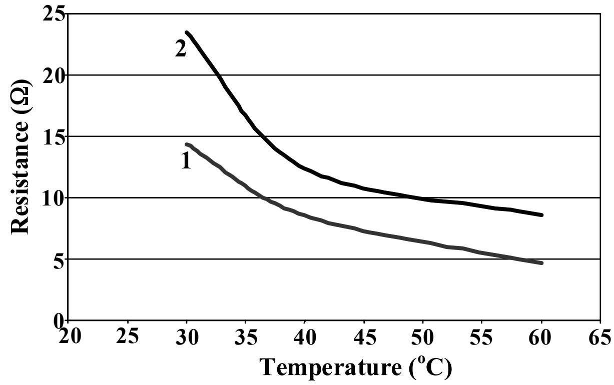

Fig. 5. Dependences of forward bias R_+ (1) and reverse bias R_- (2) resistances of the OND film deposited at 123 g on temperature.

123 g – 277 g. It means resistance is not determined by geometrical parameters of the samples only but by intrinsic conductivity of the organic semiconductor as well. Obviously in the process of deposition of the films at 1107 g some kinds structural changes took place that lead to decrease of mobility or concentration of charge carriers in the material.

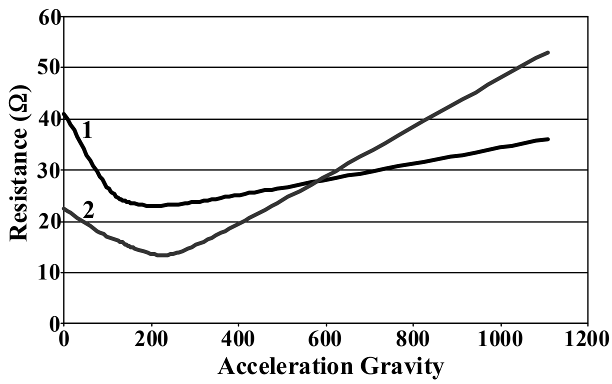

Fig. 6. Dependences of forward bias R_+ (1) and reverse bias R_- (2) resistances of the OND films on acceleration at T=30°C .

Figures 7 and 8 show dependences of rectification ratio (RR), as a ration of forward to reverse currents at equal values of applied voltages, on temperature for samples deposited at 1 g and 1107 g and on acceleration at 40°C and 60°C respectively. It is seen that RR decreases with temperature and acceleration as well.

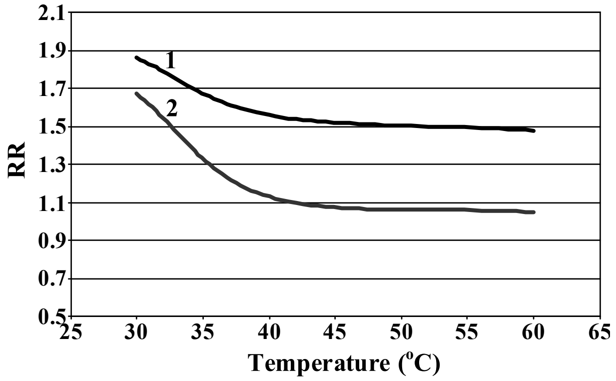

Fig. 7. Dependences of rectification ratio RR of the OND samples deposited at 1 g (1) and 1107 g (2) on temperature.

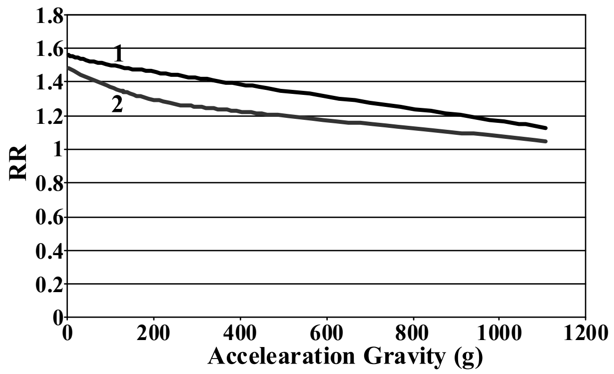

Fig.8. Dependences of rectification ratio RR of the OND samples at T=40°C (1) and T=60°C (2) on acceleration.

Figure 9 shows the voltage-current characteristics of the OND film when both electrodes of the sample were fabricated from Ga. It is seen that V-C curves are quasi-linear but symmetric unlike to the case where as electrodes nickel and gallium were used. It means that asymmetric V-C characteristics of the samples with Ni and Ga electrodes were resulted by different nature of electrodes, in particular, by work function of their (the work function for Ni and Ga are equal to 5.15 eV and 4.2 eV respectively). Really the following picture seems reflects conduction process in this case: when positive potential is applied to gallium electrode, from OND (it is p-type semiconductor) sufficiently much electrons drifted to Ga that means the same number of holes were injected into organic material. Therefore detectable conduction is observed. When positive potential is applied to nickel electrode the same situation maybe in total but the number of injected holes should be less, in comparison with the case of Ga electrode, because of higher barrier for electrons moving from OND to Ni. In the result in last case conduction should be less as in previous one.

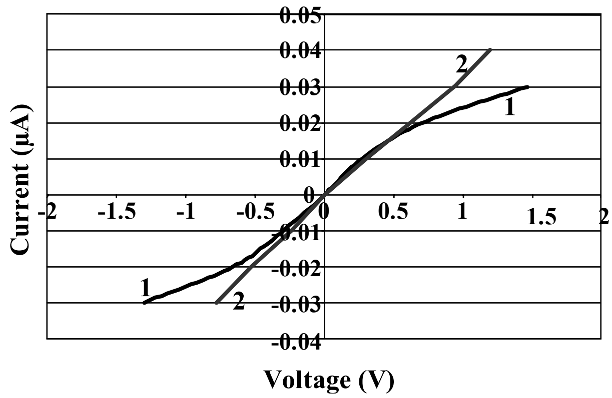

Fig. 9. Voltage-current characteristics of OND films deposited from solution at 1 g (1) and 123 g (2) measured with two Ga electrodes at T=30°C.

It is known that rectification character of voltage-current characteristics of semiconductors is resulted by non-linearity of the V-C dependences [13]. In some cases non-linearity of V-C characteristics may reach of very high values as in organic semiconductor long chain alkyl derivative which has dinitrobenzene meiety (acceptor subunit) and dihydrophenazine (donor subunit) bridged by a methylene group with constant distance and bond angle [14]. Really V-C characteristics of the OND are quasi-linear or in the first approximation are linear and are like to the characteristics of the semiconductor samples with ohmic contacts [13]. The observed V-C characteristics may be explained with conception of space-charge-limited currents (SCLC) at the presence of two different kinds of metallic electrodes. At relatively low voltages the SCLC V-C characteristics are in the domain of the linear dependence, *i.e.* Ohm's law [1,2]. The Ni-OND-Ga samples from one hand like to ohmic resistor but from the other hand they have asymmetric voltage-current behavior – like to diode. So the information obtained in the research may be used in the development of organic semiconductor diodes with linear forward bias V-C characteristics that is especially important in order to decrease of non-linear distortions in the low voltage domain.

Conclusions

- Organic semiconductor orange nitrogen dye thin films were deposited from solution in distilled water at different gravity conditions (accelerations were from 1 g up to 1107 g) by centrifugation process at room temperature.
- It was determined that voltage-current characteristics of these p-type samples were quasi-linear, asymmetrical with slightly rectification behavior. The characteristics were investigated in temperature interval from 30°C to 60°C.
- It was found that resistances of the samples decrease monotonously with temperature but with acceleration they show minimum around of 123 g – 277 g. The resistance of the samples was less at positive potential applied to Ga in comparison with the one applied to Ni.

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