

Impact of UV radiation on sensing properties of conductive polymer and ZnO blend for NO₂ gas sensing at room temperature

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Abstract—In this paper we present an investigation on UV radiation impact on an organic-inorganic blend made from a conductive polymer (regio-regular poly(3-hexylthiophene) (rr-P3HT) and a zinc oxide (ZnO) nanomaterial, which was used as the sensing layer for a chemoresistor structure. The study showed that UV radiation has a significant impact on the dynamics of the response of the studied sensor, which can be a significant element to improve the operation of such a sensor at room temperature.

Nitrogen oxides (NO_x) are one of the very harmful compounds polluting the environment, so the scientists put a lot of effort into detecting and monitoring their concentrations in the air [1]. In addition, nitrogen oxides are also products of decomposition of many explosive materials like nitroglycerine or TNT, therefore, their rapid detection is very important for social security [2].

In different types of NO₂ sensors for receptor layers materials like metal oxide semiconductors (like TiO₂, ZnO, SnO₂), and conductive polymers (like polyaniline, polypyrrole, polythiophenes) are widely used and investigated. Both regio-regular P3HT as a p-type semiconductor and ZnO as a n-type semiconductor were reported as good sensor materials for NO₂ sensing. The used materials show a good response to low concentrations of oxidizing gases such as NO₂. Moreover, literature reports that UV radiation has influence on sensor response for NO₂ gas sensing [3-4]. Both materials can be mixed together, creating a bulk heterojunction blend [5-6], which can significantly improve gas sensing properties. Bulk heterojunction materials were widely used for different microelectronic devices such organic solar cells or OLEDs and have been well described in literature in recent years [7-9]. However, the bulk heterojunction layer as a gas sensing layer has been rarely reported in recent years, particularly in studies on sensor response dynamics or gas detection threshold [10].

The object of this study is an investigation of the impact of near UV radiation on NO₂ gas sensing

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properties of an organic-inorganic blend used as the sensing layer for a chemoresistor.

The interdigital transducers (IDT) were fabricated on a n-doped (0.02 Ω/cm) Czochralski (CZ)-grown silicon wafer with a thermal SiO₂ 200 nm dielectric layer. Electrodes (20 nm of chromium and 100 nm of gold) were fabricated by a physical vapor deposition method after the photolithography process. The width of the electrode was 3 μm and the distance between the electrodes was 20 μm. The substrate platform (Fig. 1a) was designed in such a way that in the future, by embedding the gold layer as a gate electrode from the bottom of structure, it could be used as an organic thin film transistor.

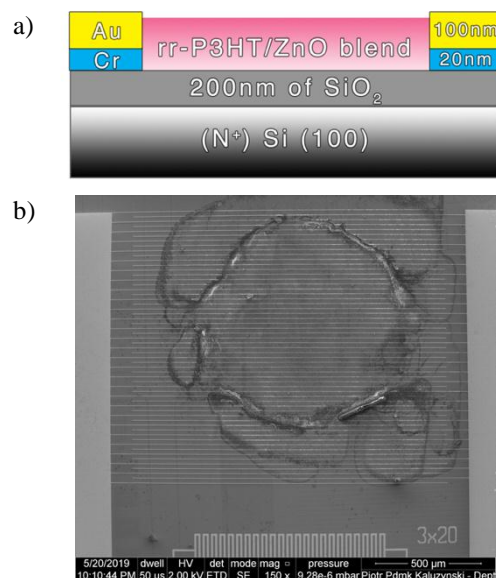


Fig. 1. a) Schematic diagram of an elaborated chemoresistor sensor, b) SEM image of elaborated chemoresistor structure.

2.5 mg of conductive regio-regular P3HT polymer was solved in 1 ml of chloroform (CHCl₃, POCh) and mixed together with 1 mg of zinc oxide nanomaterial dispersed in 5 ml of chloroform (CHCl₃, POCh) using 30 min

ultrasonic stirring. The polymer – ZnO blend was applied on the substrate using two methods. First was the airbrush method with N₂ gas, as a carrier gas, through a thin Teflon mask with hole (1000 μm diameter) and is shown in Fig. 1b. The second method was drop coating – 0.1 ml of suspension was dropped onto the IDT and dried in ambient conditions. Both elaborated structures were left to dry for 12 hours in a laminar chamber. After drying, the structures were purged with pure nitrogen to remove any non-adhering material and were connected to a chip feed-through using an ultrasonic bonding method with a 25 μm gold wire. Bonding procedure was realized using 53XX-BDA, F&K DELVOTEC wire bonder. Morphology and roughness of obtained blend thin film and ZnO distribution were investigated using SEM (Inspect S50, FEI, USA).

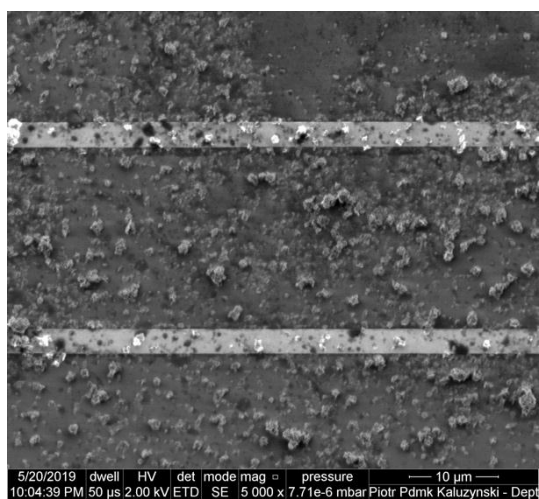


Fig. 2. SEM image of chemoresistor sensor layer elaborated with drop coating method.

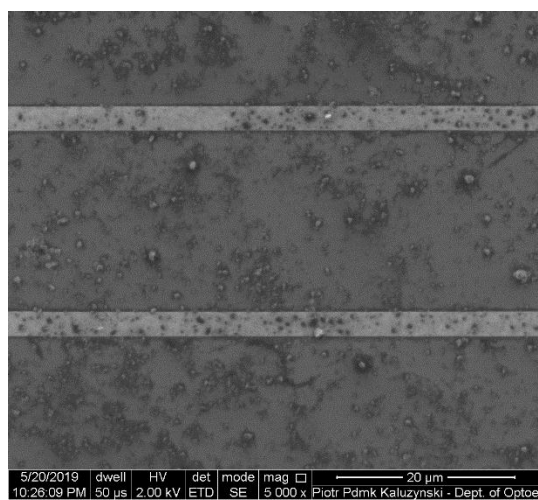


Fig. 3. SEM image of chemoresistor sensor layer elaborated with airbrush method.

The SEM images (Fig. 2 and Fig. 3) of the produced structures show a significant difference in the morphology and topography of the produced layer resulting from various methods of depositing the organic-inorganic blend. The layer created using the drop coating method contains significantly more ZnO nanoparticles than the layer produced by the airbrush method, in which the layer predominates rr-P3HT and the amount of deposited ZnO molecules is smaller. A significantly larger number of nanostructural ZnO particles in drop coated layer make this layer highly expandable, and thus it has a very large active surface for the detection of gas molecules. Moreover, zinc oxide makes local agglomerates of flower-like structures, which also strongly expands the sensory area (Fig. 2). On the other hand, the airbrushed structure is more uniform and thinner than the drop coated layer (Fig. 3).

The gas measurement system was built with the Agilent 34970A as a resistance meter of the sensor active layer. All measurements were done at room temperature (24°C), measured by Shimaden SR94 using a Pt100 sensor. The measurements were carried out in a gas chamber under N₂ as a carrier gas flow in dark conditions and under UV light illumination (LED, λ = 390 nm) and under 1, 5, 10 ppm of NO₂ gas. The gas sensing measurement setup is presented in details elsewhere [11].

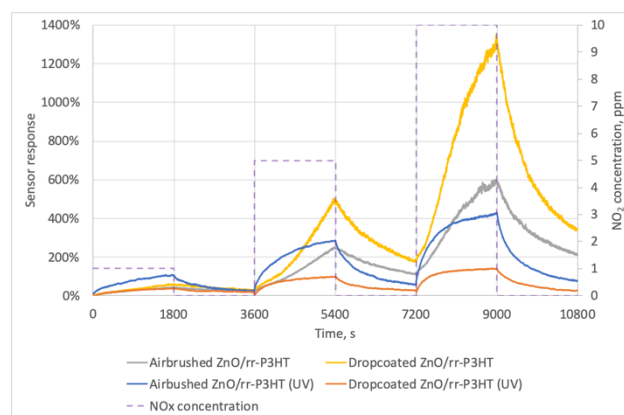


Fig. 4. Summary graph of elaborated sensor response for different NO₂ gas concentrations.

In all cases we observed a resistance drop of the fabricated sensors, during the reaction with NO₂ gas, which is characteristic for a p-type semiconductor. This proved that the conductivity of the structures is determined by the rr-P3HT polymer. The sensor response (marked as R) was calculated by using the below formula:

$$R = \left(\frac{R_a}{R_g} - 1 \right) \cdot 100\% \quad (1)$$

where R_g was the measured resistance in the target gas (NO_2) and R_a was the measured resistance in the carrier gas (base line value for N_2 gas resistance). Equation (1) represents the percentage sensor response for gas exposition (respectively for 1, 5 and 10 ppm NO_2 in N_2 carrier gas).

Obtained measurements results (Fig. 4) show that there is a significant influence of UV radiation on dynamic behaviour of the sensors (represented by the red and blue lines). The yellow and grey lines represent the sensor response without UV stimulation of the sensing layer. The purple dashed line represents NO_2 gas concentration in the N_2 carrier gas and is assigned to the right vertical axis of the presented graph. For lower concentrations of NO_2 (1 ppm), UV radiation increases the sensor response for both drop coating and airbrush deposition method, and also faster signal saturation is observed, and thanks to this the response time is shorter. Moreover, we observed that the amount of ZnO nanoparticles deposited on the sensing layer stronger affects the sensor response under UV radiation for a drop coating method than an airbrush method. This is due to the n-type conductivity of ZnO nanoparticles, which exposed to UV light generates free electrons able to reduce the holes number in P3HT via the recombination process.

In conclusion, it can be stated that there is a direct influence of UV radiation on the sensor layer sensing performance, especially the improvement of sensor dynamics and reduction of baseline drift. The obtained results clearly show that the proposed blend of materials activated by UV radiation has great potential for room temperature NO_2 sensing applications.

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