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Study of NO_2 Sensing Properties of UV Activated Graft Comb Copolymer and ZnO Blends in ppm and sub-ppm Range at Room Temperature [†]

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Abstract: n this work, novel organic-inorganic blend, made from PEGSil (Poly(dimetylsiloksan)-co-[poli(metylohydrosiloksane)-graft-2-winyl-poly(3-heksylthiophene)]-co-[poly(dimetylsiloksane)-graft- metakrylane ethere metylene poly(etylene glicole)]]) mixed with zinc oxide nanomaterial was studied as the sensitive layer for the nitrogen dioxide (NO_2) resistance gas sensor application. Moreover, the PEGSil graft copolymer material was tested in two variants, defined by side-chain length of P3HT: shorter hexane fraction (H) and longer chloroform fraction (CH). Elaborated organic-inorganic blend was deposited on interdigital transducers (Au on Si/SiO_2) by drop coating method from chlorobenzene based mixture. Sensor response characteristics to different concentrations of NO_2 (1-10 ppm) in N_2 carrier gas and synthetic air were measured and compared. Measurements were done at room temperature with UV light charge carriers activation. What is more, measurements for low gas concentrations (50-500 ppb) were done and analyzed. Obtained results shows that the sensitivity of fabricated sensors is about 6.8% per 1 ppb for hexane fractions of PEGSil and 9.3% for chloroform fractions in the concentration range from 50 to 200 ppb of NO_2 in N_2 carrier gas. This results show that blend of these materials have a huge potential as a sensing layer for NO_x low concentration sensing.

Keywords: gas sensor; nitrous oxides; UV activation; organic-inorganic; material blend;

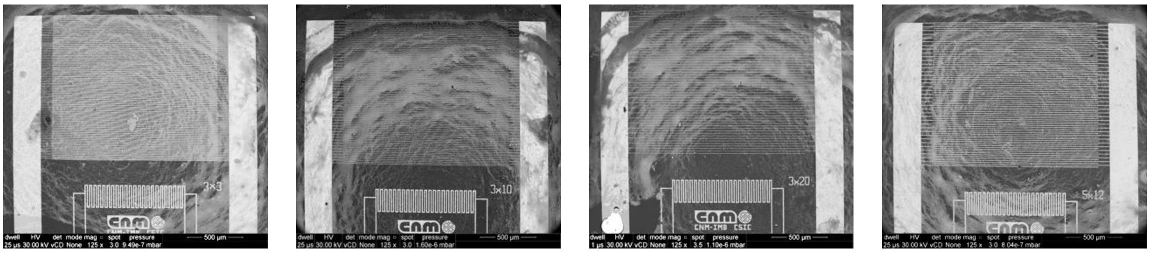
1. Introduction

The detection of nitrogen dioxides (NO_2), which are one of the most common air pollutants, is very important due to its high toxicity. NO2 sensors are used at monitoring of atmospheric air or for e.g. detection of explosive vapors [1]. Most popular sensors that are used for NO2 sensing are chemoresistive gas sensors based on metal oxides (MOX) inorganic semiconductor materials such as TiO_2, ZnO (n-type semiconductor) and others [2]. Main advantages of these materials are long-term stability and high sensitivity, but they operate at relatively high temperatures (ca. 200 °C) [3]. On the other hand, conductive polymers began to be used recently as a sensor layer, in particular polyaniline, polythiophene and their derivatives [4] like poly(3-hexyltiophene) (p-type semiconductor). Polymers showed good sensitivity, short response time and can operate at room temperature [5]. However such polymers exhibit poor processability and short-time stability for sensing applications. Both of these materials can be mixed together, creating bulk heterojunction blend, which allows to combine their material advantages and functionalization of the produced sensor layers [6,7].

Object of this study is an investigation of the organic-inorganic blend of PEGSil polymer and ZnO nanomaterial as a sensing layer for ppm and sub-ppm NO_2 gas detection at room temperature and under UV irradiation.

2. Materials and methods

The synthesis of both shorter hexane (H) and longer chloroform (CH) fractions of PEGSil (Poly(dimetylsiloksan)-co-[poli(metylohydrosiloksane)-graft-2-winyl-poly(3-heksylthiophene)]-co-[poly(dimetylsiloksane)-graft- metakrylane ethere metylene poly(etylene glicole)]]), were obtained using the method described in the patent application [9]. The graft comb copolymers were studied and their properties were described in literature [8]. The interdigital transducers (IDT) were fabricated on a n-doped Czochralski (CZ)-grown silicon wafer with thermal SiO_2 200 nm dielectric layer. Photolithography and physical vapor deposition methods were used to fabricate the electrodes on interdigital transducers. 20 nm of chromium (Cr) was evaporated on substrate, and then 100 nm of gold (Au) film as the electrodes, with channel length of 1500 μm. Four variants (Figure 1) of the transducers were made, which were divided according to the width of the electrode (W) and the distance (D) between them: 3 × 3 μm (W × D), 3 × 10 μm, 3 × 20 μm and 5 × 12 μm. The IDT were designed in such way as to be used as a substrate for organic thin film transistor in future research, after embedding a gate electrode at the bottom of the substrate by PVD method.



(**a**) (**b**) (c) (d)

Figure 1. SEM representative images of elaborated PEGSil CH/ZnO blend sensor structures, divided by electrode width and distance between electrodes: **(a)** 3 × 3 μm (W × D), **(b)** 3 × 10 μm, **(c)** 3 × 20 μm, **(d)** 5 × 12 μm.

The organic-inorganic blend was prepared by mixing together conductive graft copolymer with zinc oxide nanomaterial as a suspension for fabricating thin film layer by drop coating method. 1 mg of ZnO obtained by hydrothermal method [10,11] was dispersed in the 5 ml of chlorobenzene using 30 min ultrasonic stirring. 2.5 mg of PEGSil polymer was dissolved in 1 ml of chlorobenzene, using 30 min ultrasonic stirring. Both solutions were then mixed together using 30 min ultrasonic stirring. Prepared organic-inorganic blend was applied on the IDT substrate using drop coating method–6 μL of solution was dropped on each variant of IDT and left to dry on the heater in laminar chamber for 12 hours. After the drying process, the coated IDT structures were purged with pure nitrogen to remove any non-adhering materials. Fabricated structures were placed on a Al_2O_3 heater and connected to a chip feed-throughs, using ultrasonic bonding method with 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).

The tests of elaborated structures were carried out at different gaseous atmospheres at room temperature and under UV irradiation. As a resistance meter of the sensor active layer, a multi-switch unit 34970A (Agilent, Santa Clara, CA, USA) was used within the range of 100 MΩ, where the current source of 500 nA is used. In all cases, resistance measurements were done in room temperature (23 °C), which was measured by Shimaden SR94 using a Pt100 sensor. Measurements were carried out under UV light illumination (LED, $\lambda = 390$ nm). Preparation of gas mixtures was done by gas server based on mass flow controllers controlled by LabVIEW environment. The measurements were divided according to the carrier gas used: pure nitrogen or synthetic air. The following doses of nitrogen dioxide were used: 1, 2, 5, 10 ppm of NO_2 (standard mixture of NO_2 100 ppm in N_2) for each measurement cycle. In addition, low gas concentration measurements were made, starting with a 50 ppb dose with a 10 ppb incrementing step up to 200 ppb to determine the sensitivity characteristics of the sensors. The detailed gas sensing measurement setup is presented elsewhere [9].

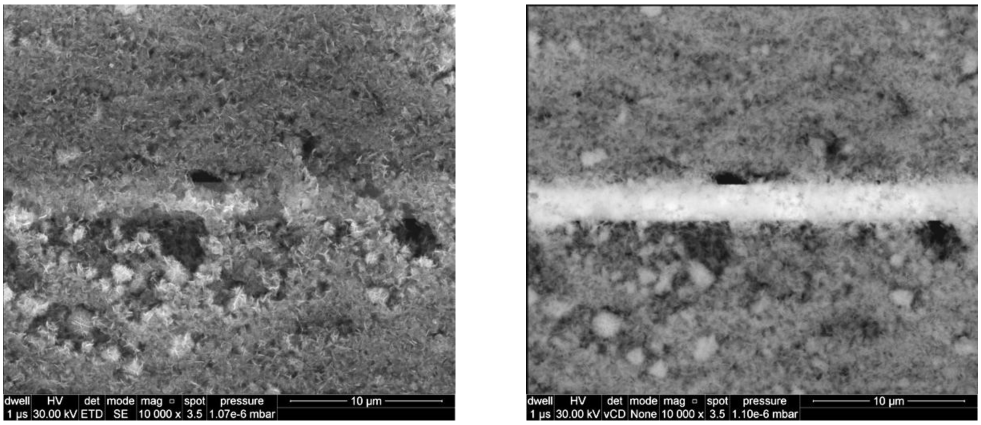
The sensor response (R) was calculated by using the formula below:

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

Where R_a was measured resistance in carrier gas (base line value) and R_g was resistance measured in target gas (NO_2).

3. Results and discussion

Sensor layer morphology and topography was investigated using scanning electron microscopy and is presented on Figure 2a and Figure 2b. Applied sensing layer have good adhesion to the substrate and shows uniform distribution of ZnO grains nanostructures. ZnO nanostructures consist of nano- and micro-bars, and nanorods, which agglomerate locally shaped in a flower-like forms, which greatly affects the active sensor surface.



(**a**) (**b**)

Figure 2. SEM images of fabricated sensor (3 × 20 μm) layer, **(a)** ETD image and **(b)** high-contrast detector (vCD).

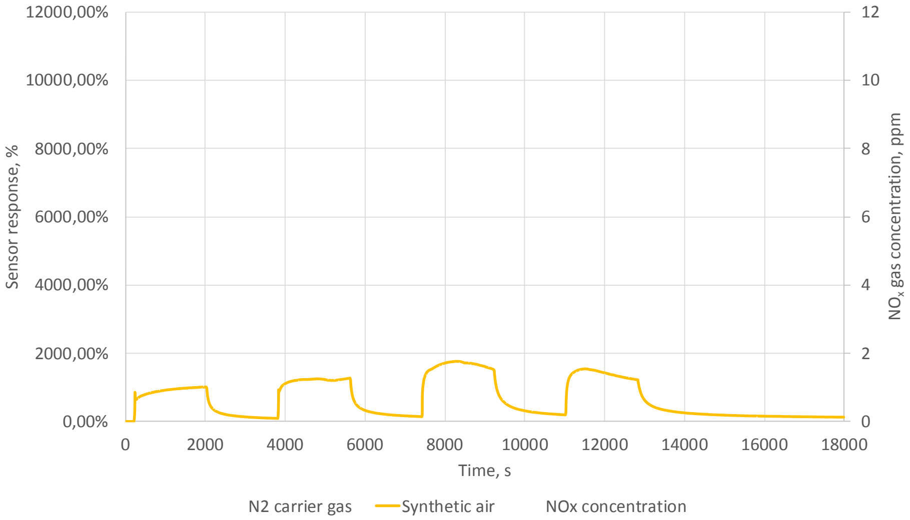


Figure 3. Sensor (3 × 20 μm) response graph of 1, 2, 5, 10 ppm of NO_2 in N_2 (blue line) and synthetic air (yellow line) carrier gas at room temperature and UV irradiation.

Figure 3 shows that the sensor response, for NO_2 gas exposition is significantly better for in case, where the carrier gas was N_2. From a practical point of view, such measurements should be also made in an air atmosphere, so synthetic air mixture was used as a carrier gas. The measurements shows that the value of the sensor response in synthetic air is lower than for N_2 atmosphere, but is still clear enough in relation to the sensor baseline that the functionality of the sensor is preserved (signal change over 1000% for 1 ppm of NO_2). Moreover the measurements also show that the sensor reaches its saturation level faster in synthetic air than in nitrogen carrier gas. This is due to the presence of oxygen in the gas mixture. Baseline drift is smaller for synthetic air carrier gas. As commercial sensors work in an air atmosphere, the further work was focused on studying the gas detection properties of two variants of PEGSil used: hexane (H) and chloroform (CH) fraction.

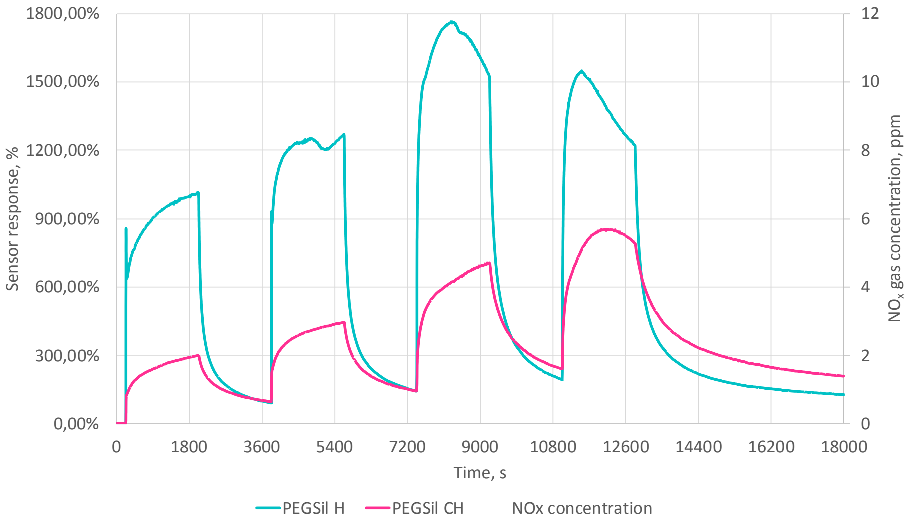


Figure 4. Sensor (3 × 20 μm) response graph of 1, 2, 5, 10 ppm of NO_2 for PEGSil H/ZnO blend (magenta line) and PEGSil CH/ZnO blend (cyan line) in synthetic air at room temperature and under UV irradiation.

Figure 4 shows that the sensor response of PEGSil H/ZnO material blend is more favorable because the response values are significantly higher than for the CH fraction, and baseline drift is comparable. It can be seen that as the NO_2 concentration increases, the decrease in sensor response signal may be due to the dominance of nanostructural ZnO in this type of material blend. At first, after the gas supply, ZnO has a majority share in the sensor layer response, then the polymer begins to dominate by adding energy carriers due to the interaction with the gas environment, as a result of which the resistance decreases and thus the sensor response.

In addition, measurements were made for a very low NO_2 concentrations N_2 carrier gas at room temperature and under UV irradiation. A measurements from 50 to 200 ppb were carried out with an incrementation step of 10 ppb in order to determine the sensor calibration curve and the detection limit of the structures made. The linear characteristics were fitted to the designated points and are presented in the Figure 5. It is worth emphasizing the good linearity of the determined characteristics, because R^2 is at a level better than 0.99. It can be stated that PEGSil CH/ZnO material blend will saturate faster, while H fraction will saturate slower. The main advantage of the H fraction will be the lower detection threshold for NO_2 in N_2. The signal change for the CH fraction has been determined and is equal to 9.30% per 1 ppb of NO_2, and for H fraction 6,80% per 1 ppb.

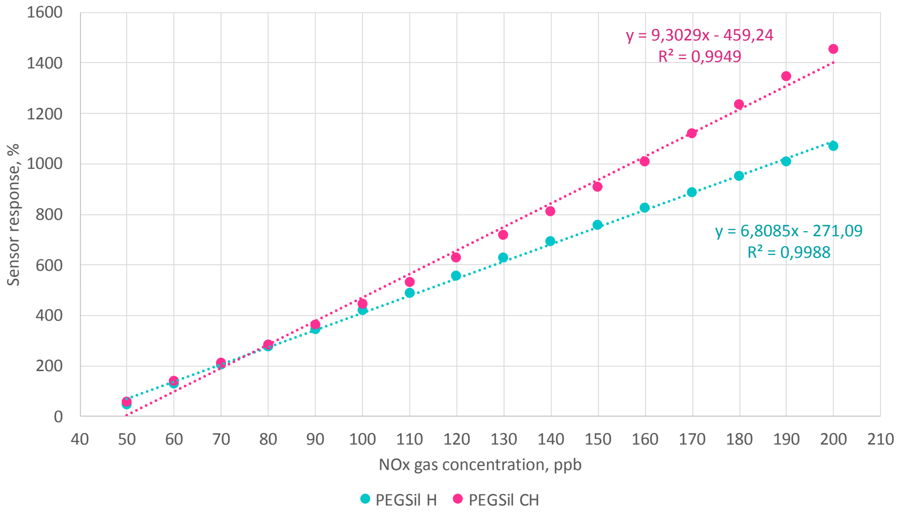


Figure 5. Sensor response graph for sub-ppm NO_2 gas concentration measurements.

Compared to our previous work [11], based solely on nanostructural ZnO, the applied sensing layer of an organic polymer (PEGSil) blend with an inorganic structured material (ZnO) significantly improved the parameters of the sensors produced, ranging from effective work at low temperatures (room temperature), through response dynamics and ending with the sensor response value itself (about 20 times greater signal change).

3. Conclusion

In this paper we presented our extensive studies of organic–inorganic material blends as a sensing layer for NO_2 gas sensor. Measurements in ppm and ppb range were made, in pure nitrogen and synthetic air carrier gas, at room temperature and under UV irradiation. Investigations presented in this paper showed that such material blend can be a promising sensory material for the detection of oxidizing gases such as NO_2. The results show that ppb level detection at room temperature is possible. However, when choosing sensor materials, you need to pay attention to individual features - baseline drift, sensor response value, signal dynamics - in our case these were the features that also differentiate both polymer fractions in terms of obtained results. The PEGSil H fraction has lower drift line

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Conflicts of Interest: The authors declare no conflict of interest

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