proceedings

Proceedings

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

Piotr Kałużynski [1],*, Marcin Procek [1] and Agnieszka Stolarczyk [2]

[1] Department of Optoelectronics, Silesian University of Technology, Krzywoustego 2 Str, 44-100 Gliwice, Poland; marcin.procek@polsl.pl

[2] Department of Physical Chemistry and Technology of Polymers, Silesian University of Technology, 9 Strzody St., 44-100 Gliwice, Poland; agnieszka.stolarczyk@polsl.pl

* Correspondence: piotr.kaluzynski@polsl.pl

† Presented at the 6th International Electronic Conference on Sensors and Applications, 15–30 November 2019; Available online: https://ecsa-6.sciforum.net/.

Published: 14 November 2019

Abstract: In this work, a 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 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 the drop coating method from a 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. Moreover, measurements for low gas concentrations (50–500 ppb) were made and analyzed. The obtained results show 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 NO_2 in N_2 carrier gas. These results show that the blend of these materials has wide potential as a sensing layer for NO_x low-concentration sensing.

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

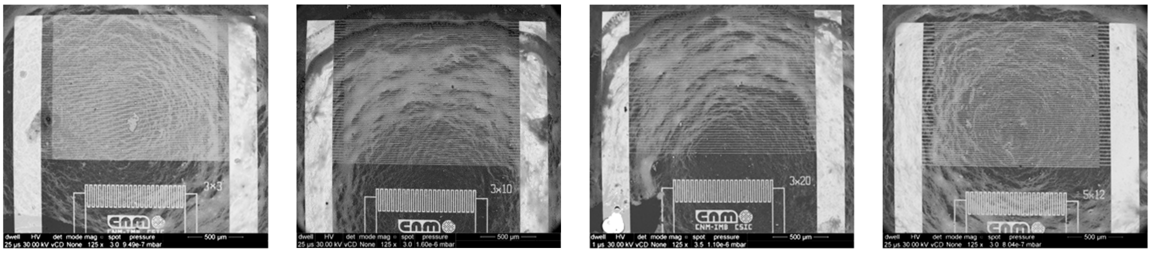
1. Introduction

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 for monitoring atmospheric air or for, e.g., the detection of explosive vapors [1]. The most popular sensors that are used for NO2 sensing are chemoresistive gas sensors based on metal oxide (MOX) inorganic semiconductor materials such as TiO_2, ZnO (n-type semiconductor) [2]. The main advantages of these materials are their long-term stability and high sensitivity, but they operate at relatively high temperatures (ca. 200 °C) [3]. On the other hand, conductive polymers have begun to be used recently as a sensor layer, in particular polyaniline, polythiophene and their derivatives [4] such as poly(3-hexyltiophene) (p-type semiconductor). Polymers showed a good sensitivity, a 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 a bulk heterojunction blend, which allows to combine their material advantages and functionalization of the produced sensor layers [6,7].

The object of this study was to investigate 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)]]), was obtained using the method described in the patent application [8]. The graft comb copolymers were studied and their properties are described in the literature [9]. The interdigital transducers (IDT) were fabricated on an n-doped Czochralski (CZ)-grown silicon wafer with a thermal SiO_2 200 nm dielectric layer. Photolithography and physical vapor deposition methods were used to fabricate the electrodes on interdigital transducers. An amount of 20 nm of chromium (Cr) was evaporated on the substrate and 100 nm of gold (Au) film as the electrodes with a 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 an organic thin film transistor in future research, after embedding a gate electrode at the bottom of the substrate using the 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 a thin film layer using the drop-coating method. An amount of 1 mg of ZnO obtained by the hydrothermal method [10,11] was dispersed in the 5 mL of chlorobenzene via 30 min ultrasonic stirring. Then, 2.5 mg of PEGSil polymer was dissolved in 1 mL of chlorobenzene via 30 min ultrasonic stirring. Both solutions were then mixed together via 30 min ultrasonic stirring. The prepared organic–inorganic blend was applied on the IDT substrate using the drop coating method—6 μL of solution was dropped on each variant of IDT and left to dry on a heater in a laminar chamber for 12 h. After the drying process, the coated IDT structures were purged with pure nitrogen to remove any non-adhering materials. The fabricated structures were placed on a Al_2O_3 heater and connected to chip feed-throughs using the ultrasonic bonding method with a 25 μm gold wire. The bonding procedure was realized using a 53XX-BDA, F&K DELVOTEC wire bonder. The morphology and roughness of the obtained blend thin film and ZnO distribution were investigated using SEM (Inspect S50, FEI, Hillsboro, OR, USA).

The tests of the 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 and the meter measurement range was set at 100 MΩ, where the current source of 500 nA is used. In all cases, resistance measurements were done at room temperature (23 °C), which was measured by Shimaden SR94 using a Pt100 sensor.

Measurements were carried out under UV light illumination (LED, λ = 390 nm). The preparation of the gas mixtures was done by a 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].

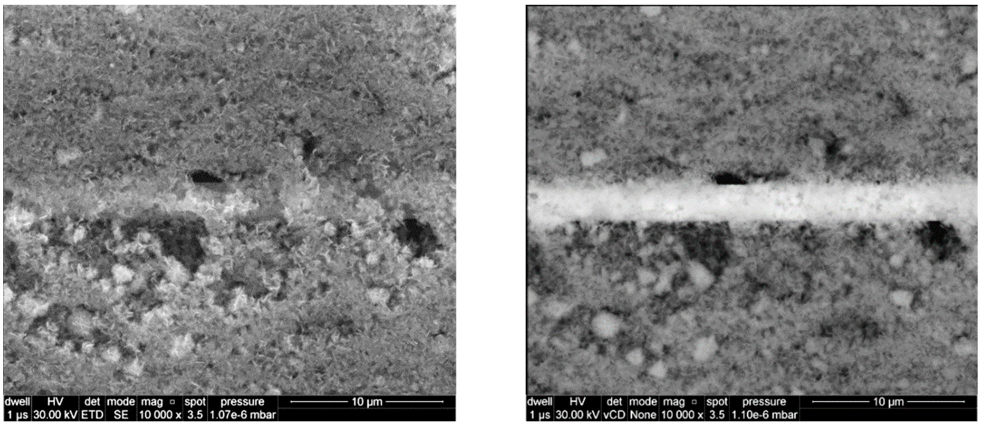
The sensor response (R) was calculated by using the formula below:

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

where R_a is the measured resistance in carrier gas (base line value) and R_g is the resistance measured in target gas (NO_2).

3. Results and Discussion

Sensor layer morphology and topography were investigated using scanning electron microscopy and are presented in Figure 2a,b. The applied sensing layer had a good adhesion to the substrate and shows uniform distribution of the ZnO grains nanostructures. ZnO nanostructures consist of nano- and micro-bars and nanorods, which agglomerate locally, shaped in a flower-like form, 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 shows that the sensor response for NO_2 gas exposition is significantly better in the case where the carrier gas was N_2. From a practical point of view, such measurements should also be made in an air atmosphere, so a synthetic air mixture was used as a carrier gas. The measurements show that the value of the sensor response in synthetic air is lower than for N_2 atmosphere, but it 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. The 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: hexane (H) and chloroform (CH) fraction.

Figure 4 shows that the sensor response of the 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 sensor response signal decreases, which may be due to the dominance of nanostructural ZnO in this type of material blend.

First, after the gas supply, ZnO had a majority role on the sensor layer response, then the polymer began to dominate by adding energy carriers due to the interaction with the gas environment, as a result of which the resistance decreases and so does the sensor response.

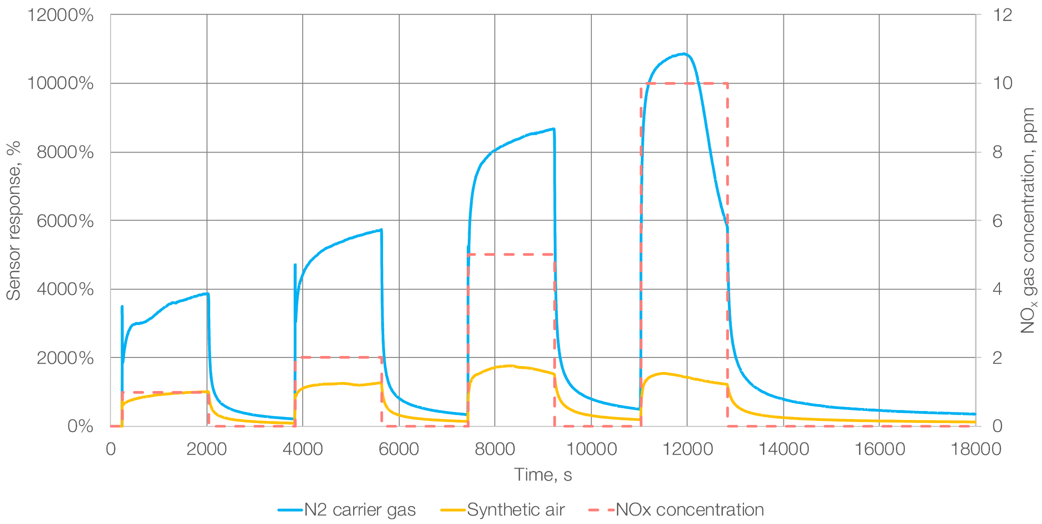


Figure 3. Sensor (3 × 20 µm) response graph of 1, 2, 5, 10 ppm of NO_2 in N_2 (blue line) and synthetic air (yellow line) carrier gas at room temperature and UV irradiation.

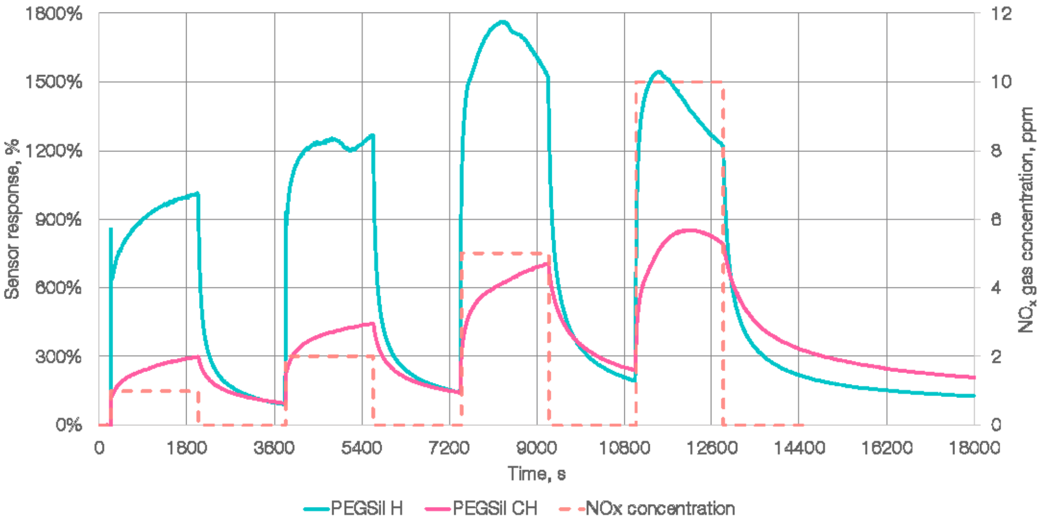


Figure 4. Sensor (3 × 20 µm) response graph of 1, 2, 5, 10 ppm of NO_2 for PEGSil H/ZnO blend (magenta line) and PEGSil CH/ZnO blend (cyan line) in synthetic air at room temperature and under UV irradiation.

In addition, measurements were made for very low NO_2 concentration N_2 carrier gas at room temperature and under UV irradiation. 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 Figure 5. It is worth emphasizing the good linearity of the determined characteristics, because R^2 is at a higher level than 0.99. It can be stated that the PEGSil CH/ZnO material blend saturates faster, while the H fraction saturates slower. The main advantage of the H fraction is the lower detection threshold for NO_2 in N_2. The signal change for the CH fraction was determined and is equal to 9.30% per 1 ppb of NO_2, and for the H fraction, 6.80% per 1 ppb.

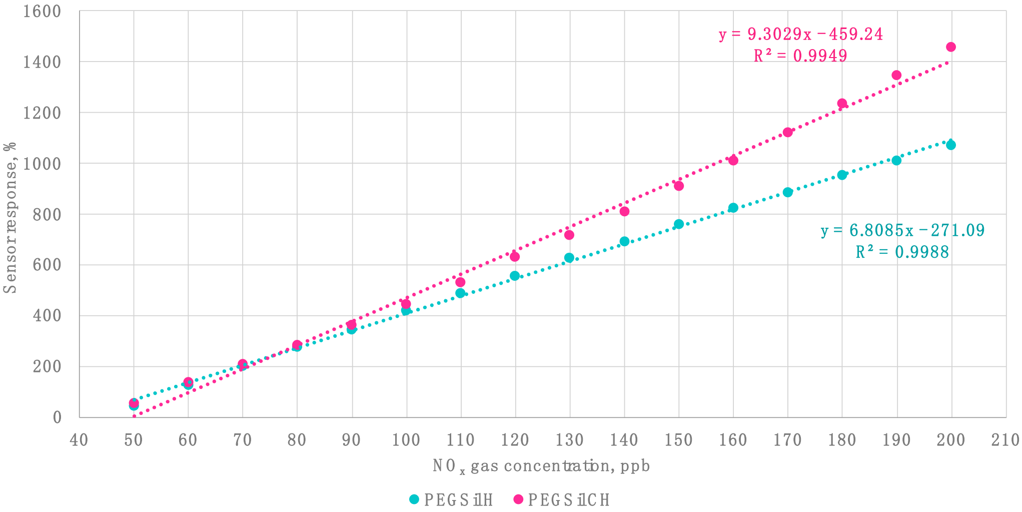


Figure 5. Sensor response graph for sub-ppm NO_2 gas concentration measurements.

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) to response dynamics and ending with the sensor response value itself (about 20 times higher signal change).

4. Conclusions

In this paper, we presented our extensive studies of organic–inorganic material blend 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. The investigations presented in this paper show that this 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, one must 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 the obtained results. The PEGSil H fraction has a lower drift line.

Author Contributions: P.K. and M.P. participated and supervised the experiments conducted in this work. A.S. acquired the funds for performing the synthesis, synthesized all investigated copolymer films.

Funding: The synthesis of graft copolymers was supported by the Foundation for Polish Science grant PARENT BRIDGE no 2011-3/8. The work was partially sponsored by the Faculty of Electrical Engineering of Silesian University of Technology within the grant BKM/567/RE4/2017, BKM/523/RE4/2018, BKM/571/RE4/2019. Agnieszka Stolarczyk gracefully acknowledges the scientific and innovative merit award no. 04/040/RGJ18/0077 of the Rector of Silesian University of Technology.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Xia, Y.; Wang, J.; Xu, J.L.; Li, X.; Xie, D.; Xiang, L.; Komarneni, S. Confined Formation of Ultrathin ZnO Nanorods/Reduced Graphene Oxide Mesoporous Nanocomposites for High-Performance Room-Temperature NO_2 Sensors. *ACS Appl. Mater. Interfaces* **2016**, *8*, 35454–35463.
2. Yunusa, Z.; Hamidon, M.N.; Kaiser, A.; Awang, Z. Gas sensors: A review. *Sens. Transducers* **2014**, *168*, 61–75.
3. Ponzoni, A.; Baratto, C.; Cattabiani, N.; Falasconi, M.; Galstyan, V.; Nunez-Carmona, E.; Rigoni, F.; Sberveglieri, V.; Zambotti, G.; Zappa, D. Metal Oxide Gas Sensors, a Survey of Selectivity Issues Addressed at the SENSOR Lab. *Sensors* **2017**, *17*, 714.

4. Bai, H.; Shi, G. Gas Sensors Based on Conducting Polymers. *Sensors* **2007**, *7*, 267–307.
5. Jarosz, T.; Kępska, K.; Ledwon, P.; Procek, M.; Domagala, W.; Stolarczyk, A. Poly(3-hexylthiophene) Grafting and Molecular Dilution: Study of a Class of Conjugated Graft Copolymers. *Polymers* **2019**, *11*, 205.
6. Djurišić, A.B.; Ng, A.M.C.; Chen, X.Y. ZnO Nanostructures for Optoelectronics: Material Properties and Device Applications. *Prog. Quantum Electron*. **2010**, *34*, 191–259.
7. Xie, T.; Xie, G.Z.; Du, H.F.; Su, Y.J.; Ye, Z.B.; Chen, Y.Y.; Jiang, Y.D. Two novel methods for evaluating the performance of OTFT gas sensors. *Sens. Actuators B* **2016**, *230*, 176–183.
8. Stolarczyk, A.; Turczyn, R.; Januszkiewicz-Kaleniak, A.; Kepska, K. The macromolecule comb-graft polymer of polydimethylsiloxane graft-conjugated polyether and a method for its preparation. *Pol. Pat. Appl*. **2014**, *407784*, RR10.
9. Procek, M.; Pustelny, T.; Stolarczyk, A.; Maciak, E. Studies of changes in electrical resistance of zinc oxide nanostructures under the influence of variable gaseous environments. *Bull. Polish Acad. Sci. Tech. Sci*. **2014**, *62*, 635–639.
10. Procek, M.; Pustelny, T.; Stolarczyk, A. Influence of External Gaseous Environments on the Electrical Properties of ZnO Nanostructures Obtained by a Hydrothermal Method. *Nanomaterials* **2016**, *6*, 227.
11. Procek, M.; Stolarczyk, A.; Pustelny, T. Impact of Temperature and UV Irradiation on Dynamics of NO_2 Sensors Based on ZnO Nanostructures. *Nanomaterials* **2017**, *7*, 312.