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B. R. Tsizh [a c], O. I. Aksimentyeva [b], M. I. Chokhan [c] & Yu. R. Portak [c]

[a] Kazimier Wielki University in Bydgoszcz, Bydgoszcz, Poland
[b] Ivan Franko Lviv National University, Lviv, Ukraine
[c] Stepan Gzytsky Lviv National University of Veterinary Medicine and Biotechnology, Lviv, Ukraine

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Sensitive Elements of Resistive Gas Sensors Based on Organic Semiconductors

B. R. TSIZH,[1,3] O. I. AKSIMENTYEVA,[2]
M. I. CHOKHAN,[3] AND YU. R. PORTAK[3]

[1]Kazimier Wielki University in Bydgoszcz, Bydgoszcz, Poland
[2]Ivan Franko Lviv National University, Lviv, Ukraine
[3]Stepan Gzytsky Lviv National University of Veterinary Medicine and Biotechnology, Lviv, Ukraine

We investigate the influence of polar gases on the electric resistance of oriented thin films of pentacene, cobalt phthalocyanine, cobalt chloride phthalocyanine, and methyl red organic dye obtained by thermo-vacuum deposition. It is determined that, under the action of ammonia and ethanol, a decrease of the electric resistance of thin films will be in progress by $10^3 \ldots 10^5$ times at a stable response signal and will give the possibility to use a simplified construction of gas sensors as a result of the absence of the heating of elements. The investigated films may be used as sensitive elements of gas sensors in the processes which accompany the ethanol evolution or for monitoring the product freshness by the pressure of ammonia which evolves from proteins during the products go bad.

Keywords Electrical resistance; gas sensor; organic semiconductor; sensitive element

Introduction

The development of simple and low cost sensors for monitoring the gas environment is of great necessity because of the bad ecological situation, noxious conditions of work, as well as a bad quality of food and its influence on man health and safety. For this reason, an important task is the development of sensitive elements which give a response to the low concentration of gases in food industry processes (for example, ethanol vapors in confectionery or alcohol drink production), in perfumery preparation, or monitoring the environment during the preservation of protein products for the food freshness estimation. Besides the well-known gas sensors with sensitive elements based on inorganic semiconductor films [1–5]), a great attention is paid to organic semiconductor sensors – molecular crystals [6–10] and conducting polymers [4,11,12]. Sensors of such a type are functioning at room temperatures and do not demand a special system of heating for ensuring the work temperature within the limits of 600 . . . 900 K, as it takes place in the inorganic sensitive elements [1–5].

Address correspondence to B. R. Tsizh, Kazimier Wielki University in Bydgoszcz, 30, Chodkiewicza street, Bydgoszcz 85-064, Poland. E-mail: tsizhb@ukw.edu.pl

In the most promising application of organic semiconductors as gas detectors, the complex multiparametric sensors such as "electronic noses" [4,5,9] are actively developed. Organic thin-film transistors based on pentacene, on SiO_2 and poly(methyl methacrylate) as gate dielectrics can function as sensors of oxygen, humidity, and other gas media [8]. Oxygen sensors may be created using the photovoltaic properties of pentacene-based barrier structures [7]. However, more simple and low-cost are the sensors of the resistive type which change the electrical resistance as a result of the adsorption of various gases [5,6]. As a sensitive material for gas sensors, the phthalocyanine thin films mostly used due their high thermal and chemical stabilities. Such films reveal the highest sensitivity to NO_2. But, after the doping by metals, for example, by magnesium, a selective response changes, and the sensitivity to HCl is observed [5].

We mention a sensitivity of some molecular crystals, namely, pentacene (Pn), to polar gases which evolve from the fish products due to their destruction – sulfides, ammonia, dimethylamine, and trimethylamine are major components of the odor from decaying fish products and therefore act as markers of the unfitness for consumption [10]. On the other hand, the gas sensors formed with Pn thin films were found to exhibit a high sensitivity in the detection of NO_2 or Cl_2 by monitoring the conductivity of a thin film. The sensors based on Pn thin films initially doped with iodine could detect ppm concentrations of ammonia gas, since iodine molecules were dedoped upon exposure to ammonia, causing a reduction of the conductivity. Nevertheless, the changes of resistivity characteristics, especially the surface electrical resistance of pure thin films of organic semiconductors under the action of a polar gas such as ethanol vapor and ammonia have a lack of study.

In the present work, the resistive sensitive properties of thin films of pentacene, cobalt phthalocyanine (CoPc), cobalt chloride phthalocyanine (CoCl Pc), and the organic red methyl dye (Met) under the action of ammonia and ethanol vapors have been investigated.

Experimental

We study organic semiconductors of various types, namely, complexes of phthalocyanines with cobalt and cobalt chloride, linear polyacenes – pentacene, and organic dye – methyl red (Fig. 1). These materials were kindly given by

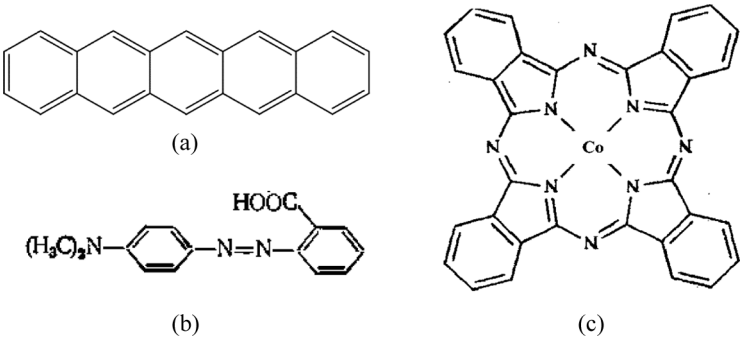

Figure 1. Chemical structure of pentacene (a); methyl red, Met (b); and cobalt phthalocyanine, CoPc (c).

Dr. Ya. I. Vertsimakha (Institute of Physics of the NASU, Kyiv) and used without an extra purification.

To provide a stable reversible response of the films, we chose a method of thermal deposition which is one of the most common methods to form films of molecular crystals in vacuum [7,13–15]. The thin films of indicated semiconductors were obtained with molybdenum evaporator at a residual gas pressure of $(3 \ldots 7) \cdot 10^{-3}$ Pa at temperatures of 373 ... 433 K. We have experimentally verified that high-quality films of organic semiconductors without heterogeneous inclusions, with properties close to those of single crystals, precipitated at low speeds of evaporation. So the deposition speed of organic semiconductors amounted to 0.5 ... 1.0 nm/s. Films with a thickness of 200–300 nm were deposited on glass substrates with nickel electrodes. The obtained condensates were homogeneous and possessed a polycrystalline structure with sizes of crystalline grains of 80–120 nm which were oriented along the *c*-axis (perpendicularly to the layer). The degree of orientation of thin films of the investigated organic semiconductors was high. For example, for Pn films, the textural level exceeded 90 percent, the texture axis dispersion angle (crystallite disorientation) was within the limits of 6 ... 10 degrees, and the texture axis angle of a deflection from the normal to the film surface was within the limits 1.1 ... 1.8 degrees.

Electric resistance measurements were carried out at room temperature (293 K) with the use of a teraohmmeter E6-13A with the range of measured electrical resistances $10^4 \ldots 10^{14}$ Ohm. The investigation of organic semiconductor film peculiarities was performed with the help of a hermetic chamber, where a sample was placed, which was connected with a water manometer and a valve for supplying the indicated gas. The resistance changes were fixed after the attainment of a stationary state (in 60 ... 120 s). Because the initial values of the surface resistance of different organic crystals can be different, we normalized for presentation the experimental values of resistances under the gas action to initial resistances for the better presentation of experimental data.

Results and Discussion

As a rule, undoped molecular organic semiconductors have high values of the dark specific electrical resistance (ρ) at room temperature [5]. The values of ρ for the obtained condensates were within the limits of $6 \cdot 10^9 \ldots 2 \cdot 10^{12}$ Ohm · cm under normal conditions. The preliminary testing of films showed that their sensitivity to acetone vapor, hydrogen sulphide, carbon dioxide, water vapor, and oxygen is significantly lower as that to ammonia and ethanol vapor. Because these gases are present in the environment of important industrial processes [4,5,10], their influence on the film surface resistance was study in more details.

During the addition of ammonia or ethanol vapor into a measuring chamber, the electrical resistance of a film is essentially decreased (by 10^5 times), as is shown in Fig. 2 and Table 1. Here, the sensitivity $S = R_0/R_s$, where R_0 and R_s are, respectively, the electrical resistances of the film in open air and at the gas addition. The response time is to 10 s at the enough low threshold of sensitivity (less than 100 Pa) was observed. Such high sensitivity and the quick establishment of a stationary response may be assigned to the interaction of the indicated gases with the surface of organic thin films [9,10].

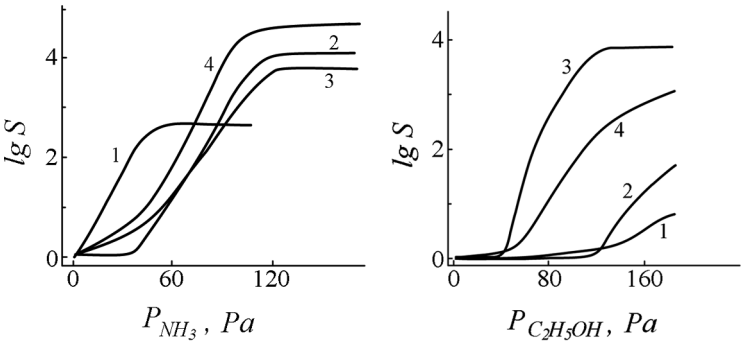

Figure 2. Logarithmic dependence of the sensitivity of films of CoPc (1), Pn (2), CoClPc (3), and Met (4) on the partial ammonia pressure (a) and the ethanol vapor pressure (b) at a temperature of 293 K.

The ammonia molecule, being present in the gas medium, can be adsorbed by the molecular crystal surface, which is accompanied with a considerable reduction of the surface electrical resistance and can testify to the formation of weak chemical bonds [10]. The interaction of ethanol molecules with the surface of organic semiconductors also causes an essential reduction of the film resistance, which is especially appreciable in the case of phthalocyanine cobalt chloride (Fig. 2b, curves 3 and 4). Such an interaction is weak and reversible. After the gas evacuation or the exposition of the films on air, the initial values of resistance returns to the initial values in the limits of 90–300 seconds, which makes it possible to provide a reversibility of sensitive elements.

By the results of our investigation, the maximal decrease of the electrical resistance under the action of ammonia (by $10^4 \ldots 10^5$ times) takes place for films of Pn, CoClPc, and Met. In the presence of ethanol vapor, the resistance decreased by $10 \ldots 10^4$ times for films of CoClPc and Met. The comparison of the sensor

Table 1. Sensor peculiarities of organic films and inorganic semiconductors

Semiconductor film	Gas	Working temperature, °C	Sensitivity threshold, Pa	Detection limit, Pa	Sensitivity, $S=R_0/R_S$	Time of response, s
Pn	Ammonia	−10 ... 50	35	125	10^4	1
CoPc	Ammonia	−10 ... 50	1	60	750	5
CoClPc	Ammonia	−10 ... 50	5	125	$7 \cdot 10^4$	6
Met	Ammonia	−10 ... 50	3	110	10^5	3
Pn	Ethanol	5 ... 35	95	>200	30	8
CoPc	Ethanol	5 ... 35	65	>300	5	8
CoClPc	Ethanol	5 ... 35	38	120	10^4	7
Met	Ethanol	5 ... 35	42	190	$3.2 \cdot 10^3$	3
ZnO (Al)	Ethanol	200 ... 500	100	$5 \cdot 10^3$	80	5
ZnO (In)	Ethanol	200 ... 500	110	$3 \cdot 10^3$	34	20
ZnO	Ethanol	200 ... 500	160	$7 \cdot 10^2$	4	100

sensitivities of organic semiconductors with those of the known zinc oxide sensors under the same experimental conditions [3] testifies to the considerable preference of organic semiconductors, especially for the determination of small gas concentrations which are out of the detection limits of oxide-based sensors (see Table 1). In view of great changes of the electrical resistance of organic semiconductors and a low threshold of their gas sensitivity (in comparison with those of most inorganic thin-film elements [1–3]), these molecular crystals can be recommended for the design of the sensitive elements of resistive gas sensors for biotechnological processes in the food industry and other branches and for the monitoring of protein food freshness.

Conclusions

The proposed sensitive elements for gas sensors of ammonia and ethanol vapor based on organic semiconductors ensure the resistance change by $10^3 \ldots 10^5$ times, which exceeds the sensitivity of inorganic sensor films by $2 \ldots 3$ orders. The high sensitivity to a gas action, low detection limit, small response time, stability of a signal, and the possibility of using a simple construction of gas sensors due to the absence of heating elements allow us to recommend the organic semiconductors (polyacenes, phthalocyanines, and organic dyes) for the development of gas sensors for the food industry processes which involve ethanol and for the monitoring of the freshness of food products by the ammonia detection.

References

[1] Paraguay, D. F., Miki-Yoshida, M., Morales, J., Solis, J., & Estrada, L. W. (2000). *Thin Solid Films*, *373*, 137.
[2] Koshizaki, N., & Oyama, T. (2000). *Sensors and Actuators B*, *66*, 119.
[3] Chokhan, M. I., Tsizh, B. R., Lasorenko, V. Y., & Aksimentyeva, O. I. (2008). *Eastern-European J. Enterprise Technologies*, *6/4*(30), 49.
[4] Wilson, S.A., Jourdain, R. P., Zhang, Q., Dorey, R. A., & Bowen, C. R. *et al*. (2007). *Materials Science and Engineering R: Reports*, *56*(1–6), 1.
[5] Hotra, Z. Yu. (Ed.) (2003). *Microelectronic Sensors of Physical Values*, Liga Press: Lviv.
[6] Minakata, T. (1995). *Polym. for Adv. Techn.*, *6*, 607.
[7] Vertsimakha, Ya., & Verbitsky, A. (2000). *Synthetic Metals*, *109*, 291.
[8] Lohani, J., Saho, P., Kumar, U., Balakrishnan, V. R., & Basu, P. K. (2008). *Pramana J. Phys.*, *71*, 579.
[9] Burlachenko, Yu. V., & Snopok, B. A. (2008). *J. Anal. Chem.*, *63*, 557.
[10] Honeybourne, L. (2000). *Journal of Chemical Education*, *77*, 338.
[11] Kukla, A. L., Pavluchenko, A. S., Kotljar, V. A. *et al*. (2005). *Sensor Electronics and Microsystem Technologies*, *2*, 42.
[12] Tsizh, B. R., Chokhan, M. I., Aksimentyeva, O. I., Konopelnyk, O. I., & Poliovyi, D. O. (2008). *Mol. Cryst. Liq. Cryst.*, *497*, 254.
[13] Bogdanova, N., Baumann, M., Bevierre, M. O., & Xie, X. (1996). *Thin Solid Films*, *1–2*, 239.
[14] Toshiro, S., Wade, S., Toshiyuki, K. *et al*. (1993). *J. Phys. Chem.*, *30*, 8026.
[15] Souto, J., De Saja, J. A., Aroca, R., & Rodriguez, M. L. (1993). *Synth. Metals*, *1–3*, 229.