Sol-gel coatings for electrical gas sensors

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The influence of volatile organic compound vapours of TiO_2 gas-sensing layers prepared via the sol-gel technique was investigated. The sol-gel-derived layers were tested in the environment of alcohols, aliphatic and aromatic compounds. Specified organic compounds caused reversible changes of the semiconductor film resistance. The response of the titania film was registered as current intensity changes versus time at different sensor operating temperatures. The results suggested that TiO_2 films prepared by the sol-gel technique can be used as chemical sensors.

Keywords: gas sensor, sensor, sol-gel layer, sol-gel technology.

1. Introduction

The sol-gel method is a simple and versatile method of obtaining metal oxide thin films. A major advantage of the sol-gel processes over the vapour phase methods is the ability to control the microstructure of the deposited film, *i.e.*, pore size, pore volume and surface area. There is observed a growing interest in employing this technology to explore novel materials for gas sensing applications. Among others, semiconducting metal oxides such as TiO_2 [1], SnO_2 [2], ZnO, Ga_2O_3 [3], WO_3 [4] and MoO_3 [5] are investigated.

Titanium dioxide shows promising gas sensing properties for various applications, so it has been extensively studied in the past decade. TiO_2, pure or doped, can find application as both optical [6] and electrochemical sensing devices. Sensors for

alcohols [7–9], reducing, or oxidizing gases (NO_2, CO, H_2, O_2) [10–13] are examples of such devices based on changes of electrical properties of the films. Sensors in the form of thin or thick films are very attractive. The main advantages of the thin film sensors are: small size, simple construction, low cost, low weight and low power consumption. Nevertheless, it is important to improve some overall properties of the sensing devices such as wide operating temperature range, high temporal stability, good accuracy, small hysteresis loop, low price, a high concentration sensing range, easy processing and reproducibility [14].

Transport facilities require the control of automotive fuel quality. Both gasoline and oil must possess good quality, otherwise they will cause an increase of pollutants emission and faster engine wear. In the fuel market, there exist illegal practices, *e.g.*, addition of different chemicals or solvents and mixing diesel oil with heating oil to increase company's profit. Therefore, it is necessary to develop a fast and inexpensive sensing system for monitoring fuel quality.

This work reports on the application of such a sensing device for detection and recognition of the various volatile organic compounds. Sensitivity of the TiO_2 layer for hexane, 1-hexanol, cyclohexane and benzene has been investigated. The electrical response of the sensor was measured by recording the change in the current intensity of the thin film made by the sol-gel technique and deposited on an alumina substrate. The signal was registered at different operating temperatures of the sensor. The characteristics of response to the compound vapours are discussed.

2. Experimental

Titania thin films were prepared from titanium *n*-butoxide (TNBT, obtained from Aldrich). TNBT was sonicated with butanol and acetylacetone (both obtained from POCH) with the molar ratios $1:20:2.3$. Distilled water was added to the solution (the ratio of $TNBT:H_2O$ was $1:0.3$) after one hour and it was further mixed for 30 minutes. The sol was aged at room temperature for 24 hours. Alumina transducer (96% Al_2O_3) with interdigital gold electrodes on one side and a Pt heater on the other side was used as a substrate. The heater allows the working temperature of the sensor to be controlled up to 500°C. The substrates were cleaned in acetone and then dried in 70°C. The films were deposited by the modified dip-coating technique. The part of substrate with electrodes and heater was immersed in the solution. The liquid was slowly poured out through the hole at the bottom of the container. The withdrawal speed was about $0.1\ \text{mm}\,\text{s}^{-1}$. Three (sample S3) or five (sample S5) layers were deposited to obtain thicker films. The next layer was deposited after 10 minutes required for drying. The titania films were annealed in the air for one hour at 600°C at a heating rate of 10°C/min.

For the purpose of measurements, a sensor plate was placed in a flow-type gas chamber (Fig. 1). The sensor connected to a power supply and a measuring device consisted of reference resistors, a digital multimeter with a data acquisition card and a PC. The electrical response of the titania layer was registered as the current intensity
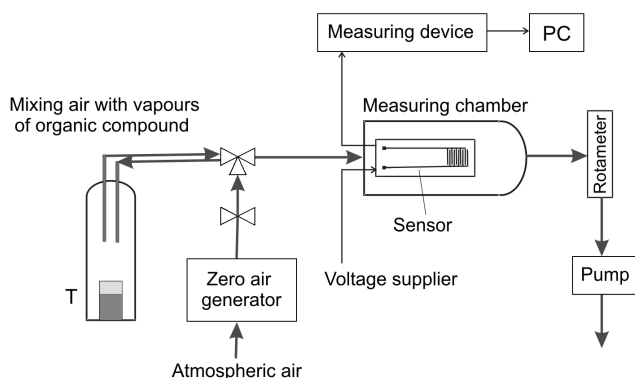
Fig. 1. Experimental setup.

was changing versus time at different sensor operating temperatures. The digital multimeter was used to transfer the data to the computer. A constant potential of 5 V was applied to the thin film. The operating temperature (275, 320, 360, 400 or 440°C) was maintained by the Pt heater operating in the DC mode.

The gaseous samples of hexane, 1-hexanol, cyclohexane or benzene (POCH) were prepared by "head space" method. Briefly, a glass vial with 2 ml of compound was placed in a "head-space" sampler installed in a thermostat at 50°C. The pure air was used as the gas carrier. Pure and dry air was generated by a device (Horiba) consisting of a compressor and cartridges filled with silica gel, activated carbon, soda lime and molecular sieves. The mass flow controller was used to set the gas flow. After one minute of gas mixing, the stream of air with organic vapours was directed through teflon hoses to the measuring chamber with the sensor and the sensor response was measured. Between the measurements, the pure air flew through the chamber.

3. Results and discussion

Figure 2**a** shows SEM micrographs of TiO_2 layer deposited three times (S3) on alumina substrate and annealed at 500°C for 1 hour. The film is sufficiently thin so the structure of the substrate can be seen. There are no cracks or scratches. In Figure 2**b**, the structure
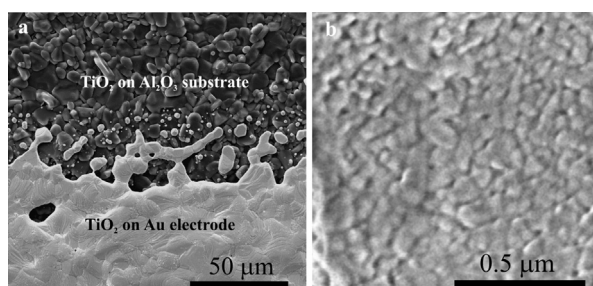

Fig. 2. SEM micrographs of: **a** – alumina substrates with gold electrodes coated with TiO_2 film (S3) and **b** – the structure of the TiO_2 film.
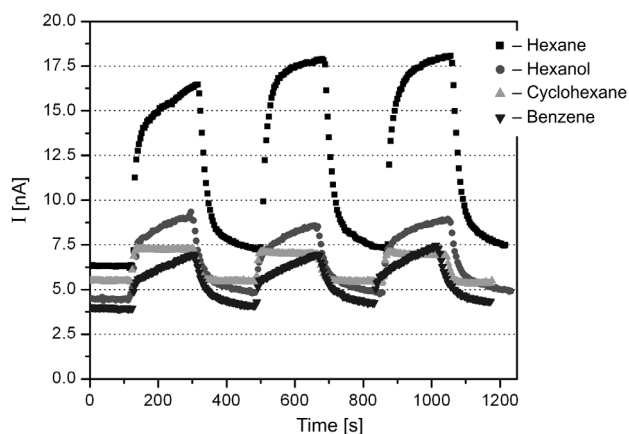
Fig. 3. Current variation for S3 sensor (three layers of TiO_2) related to exposure to different compound vapours at the operating temperature of 360°C.

of the titania film can be seen. Using other SEM photos, the thickness of the films was estimated to be approximately 300 and 500 nm for S3 and S5, respectively.

The sensor based on sol-gel-derived titania thin film has been exposed to the vapours of hexane, 1-hexanol, cyclohexane or benzene at operating temperatures of 275, 320, 360, 400 and 440°C. The current intensity changes *I* of the titania layer were registered as a function of time. Figure 3 shows the response of the S3 sensor versus different compound vapours at a temperature of 360°C, when gas pulses were introduced. The electrical characterization has revealed that TiO_2 layer is the *n*-type semiconductor (at elevated temperatures, its electrical resistivity decreases in response to the analysed gases). The sensor's signal intensity is usually repeated after regeneration and next gas injection.
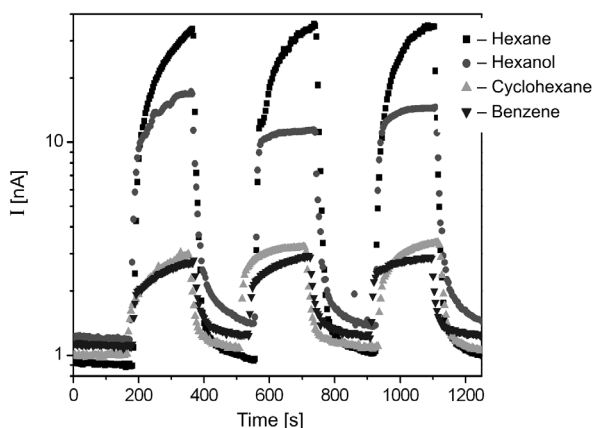

Fig. 4. Current variation for S5 sensor (five layers of TiO_2) related to exposure to different compound vapours at the operating temperature of 360°C.

For three-layer film (S3), the biggest signal change ($\Delta I = I_g - I_b$, where I_g is the current intensity at different vapours of organic compounds, registered after 180 s from the gas injection and I_b is the current intensity when the film is exposed to the pure air) was observed for hexane and smaller changes were registered for hexanol, benzene and cyclohexane. Similar results were obtained for other temperatures, only at 440°C, the relative current for hexanol was the lowest. For S5 (Fig. 4), benzene always shows the weakest signal. A higher value is observed for cyclohexane and the highest one for hexane (275, 320 and 360°C) or hexanol (at 400 and 440°C). Unfortunately, a decrease of the base line could be observed during the experiment – from 6.3 to 4.0 nA and from 1.2 to 0.9 nA for S3 and S5, respectively. This change in current intensity indicates that the film is not stable and its electrical properties vary with time. The film S5 has lower value of the current intensity in air I_b, but it has better response to hexane and

T a b l e. Statistical analysis of the gas response $R = \Delta I/I_b$ obtained for hexane and hexanol at different temperatures ($\bar{x}$ – average value, S – standard deviation, $Vx = (S/\bar{x}) \cdot 100$ – variation coefficient).

Operating temperature	Statistics	Hexane		Hexanol	
		Sensor S3	Sensor S5	Sensor S3	Sensor S5
$T = 275°C$	$\bar{x}$	2.649	1.021	1.280	20.684
	x_{min}	2.504	0.983	1.161	18.367
	x_{max}	2.908	1.053	1.422	25.808
	S	0.143	0.035	0.086	3.471
	Vx	5.4%	3.5%	6.7%	16.8%
$T = 320°C$	$\bar{x}$	1.449	2.127	1.198	15.076
	x_{min}	1.306	1.835	0.986	10.725
	x_{max}	1.570	2.490	1.393	22.548
	S	0.133	0.325	0.173	6.501
	Vx	9.2%	15.3%	14.5%	43.1%
$T = 360°C$	$\bar{x}$	1.362	36.399	0.922	11.078
	x_{min}	0.747	30.229	0.528	6.841
	x_{max}	1.549	46.152	1.477	20.496
	S	0.284	6.959	0.325	5.494
	Vx	20.9%	19.1%	35.2%	49.6%
$T = 400°C$	$\bar{x}$	1.189	22.571	0.601	7.375
	x_{min}	1.089	19.695	0.448	5.980
	x_{max}	1.263	25.345	0.844	9.582
	S	0.090	2.446	0.170	1.934
	Vx	7.6%	10.8%	28.3%	26.2%
$T = 440°C$	$\bar{x}$	0.967	12.663	0.362	3.975
	x_{min}	0.814	12.101	0.287	2.543
	x_{max}	1.125	13.692	0.564	5.616
	S	0.115	0.893	0.105	1.369
	Vx	11.9%	7.1%	29.0%	34.4%

hexanol (*e.g.*, for hexane $\Delta I_{440°C} = 100$ nA as compared to 40 nA for S3). Though, contrary behavior can be found for hexane at 320 and 275°C (*e.g.*, $\Delta I_{320°C} = 0.7$ nA and 3.5 nA for S3).

The sensor response to vapours R is defined as $\Delta I / I_b$. Statistical analysis of the results obtained for hexane and hexanol at different temperatures is presented in the Table. The average value $\bar{x}$ has been calculated from a few measurements. The highest value of R, for both gases and sensors, was registered at 275°C (the numbers with grey background in the Table), but the signal was very weak (< 1 nA) and the relative current intensity ΔI was small. For sample S5, at 360°C R is sufficiently large and it is much easier to register the signal without disturbances.

Comparing the responses for each temperature, it can be seen that R is almost every time higher for S5 (underlined numbers). Moreover, the response to hexanol is better than the response to hexane, at 275 and 320°C (double underlined numbers). Hexane changes the electrical properties of the thin film more than hexanol at higher temperatures. In the Table, variation coefficients are also presented. For these two gases, better repeatability of results is obtained for hexane.

A decrease in sensor response with temperature has been registered for hexanol, as well as for hexane, but only with S3 sample (Fig. 5). For sensor with five TiO_2 layers, R increases with temperature, it has the highest value at 360°C and then decreases. The same results are observed for benzene when both sensing plates are used. Only increasing tendency is observed with cyclohexane. All these results may be used to apply the sensing device to recognize compounds that have similar chemical structure (all molecules have 6 carbon atoms). For instance, all the compounds can be recognized at lower operating temperatures with sensor S3 and sensor S5 will easily distinguish hexane from cyclohexane and benzene.

The response time of the sensor to vapours of volatile organic compounds was relatively short. For instance, it was found to be about 70 s for hexane at 440°C and the time required for the sensor to regenerate was estimated to be 75 s. The current
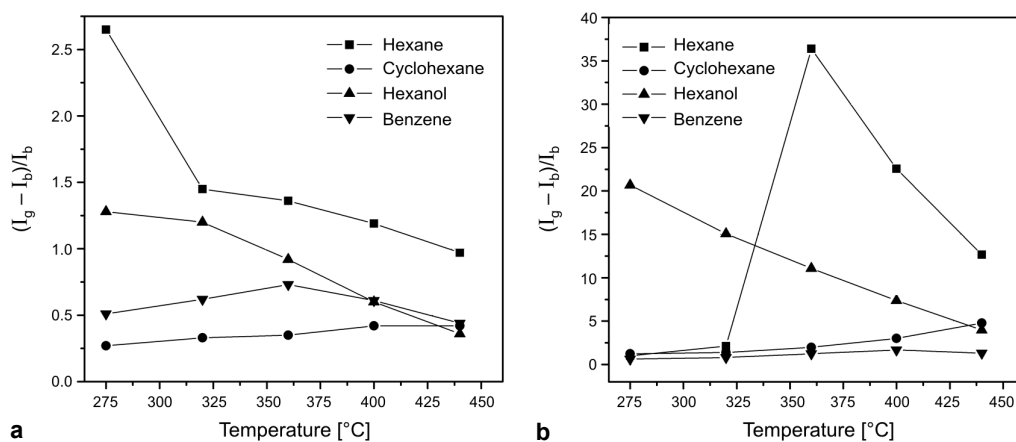

Fig. 5. Response of sensor S3 (**a**) and sensor S5 (**b**) at different operating temperatures.
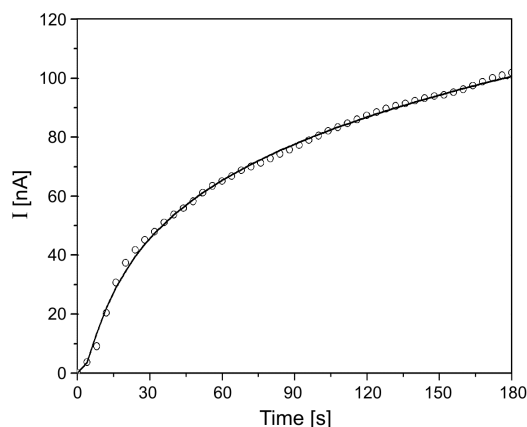
Fig. 6. Current variation for S5 in hexane at the operating temperature of 440°C (○) and the mathematical model (—).

intensity grows rapidly for about 30 s from the gas injection and later the increase is slower (Fig. 6). One of the mathematical models:

$$I = b_0 \quad \text{for} \quad t = 0,$$

$$I = b_0 + b_1^{b_2 \ln(t) + \frac{b_3}{t} + b_4}$$

can be assigned to this variation. For sample S5 in hexane at 440°C, the parameters have the following values: $b_0 = 8.354$, $b_1 = 1.56$, $b_2 = 0.68$, $b_3 = -20.25$, $b_4 = 6.93$, and $R^2 = 0.999$ (for $t = 0$ s $\Rightarrow I = I_b$ and for $t = 180$ s $\Rightarrow I = I_g$). As can be seen, the line corresponds well to the experimental data.

4. Conclusions

The sol-gel-derived TiO_2 thin film was used to obtain sensor array for volatile compound recognition. The properties of this sensor are presented below:

– the sensor investigated can be used to recognize organic vapours of similar organic compounds;

– the gas response is usually the highest for hexane and the lowest for cyclohexane and benzene at every operating temperature tested;

– for hexanol, the sensor response is the largest at 275°C, for benzene at 360°C and for cyclohexane at 440°C. The best temperature for hexane recognition is at 275°C for sensor with three layers of TiO_2 and 360°C for plate with five layers;

– unfortunately, the electrical properties of the film are not stable. A decrease of current in the pure air during measurements was observed;

– the response-time for hexane was found to be about 70 s and the time required for the sensor regeneration – 75 s.

The results obtained are very promising. The sensor can recognize not only an individual compound, but also the mixtures – it can distinguish between diesel and heating oil (results not published). Although, the film stability must be improved and the concentration measurements have to be made.

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