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Thin film nanocomposite electrodes for electrochemical sensors

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Abstract

In this paper, we present highly sensitive thin film nanocomposite electrodes for electrochemical sensors. The nanocomposite electrodes are obtained on the porous PTFE substrate by magnetron sputtering co-deposition of the graphite/platinum target. As a result, the thin film nanocomposite electrode consists of an amorphous carbon matrix which includes platinum metal nanoclusters (a-C/Pt). The electrochemical gas sensors with the developed electrodes are produced and tested in several gas atmospheres. Experimental results demonstrate that a-C/Pt has higher sensitivity as compared to traditional powder catalysts.

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Keywords: electrochemical sensors; magnetron sputtering; nanocomposite electrode.

1. Introduction

The development of cheap, tiny and efficient gas sensors that are able to detect toxic and hazardous gases is a topic of high priority in the scope of the life safety issues. In fact, a hazardous gas leaks at industrial facilities are typically detected using bulky and power hungry systems based on catalytic/semiconductor [1, 2] and optical technologies [3]. Besides life safety, the problem of energy-saving and resource-saving is important for autonomous sensing systems, e.g. wireless sensor networks

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[4]. The technology of thin film nanocomposites results in the improved sensor reproducibility, while the production costs are kept low [5][6]. This is achieved due to the fact that a whole array of electrodes can be produced in a single technological process.

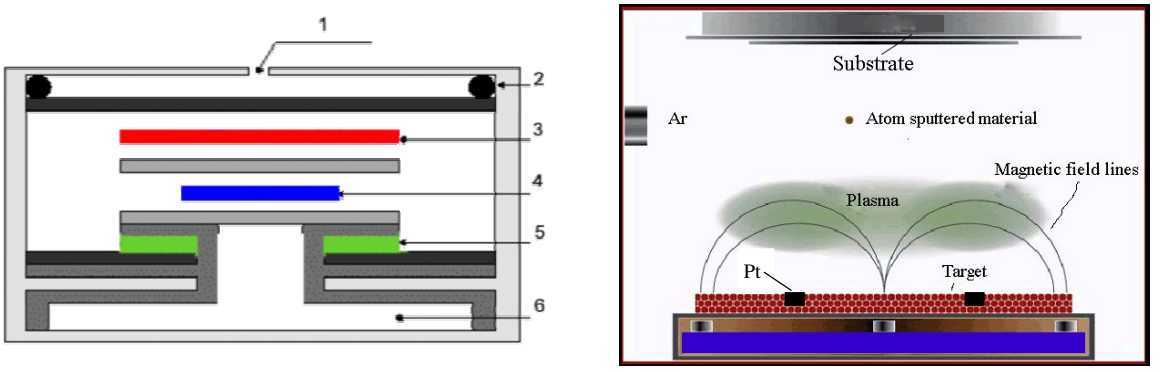
The novelty of this work is in designing of highly selective electrochemical sensors for continuous monitoring of carbon monoxide (*CO*) and hydrogen sulfide (H_2S) in the gaseous environment. The selectivity of the sensor is provided by the thin film carbon-platinum electrode which enables the oxidation reaction at predefined potential. This solution prevents other oxidation-reduction reactions happen on the working electrode in aquosystem. A distinctive feature of our approach is that the platinum clusters are patterned together with the carbon film growth at the time of deposition.

We first describe the sensor fabrication process and then evaluate its performance in terms of selectivity and response.

2. Sensor Design

2.1. Electrochemical cell

Fig. 1 presents schematic of the electrochemical cell used in this work. It is a three-electrode cell which enables investigating of electric current intensity depending on voltage on the working electrode. This cell is designed for detecting and controlling of hazardous gases concentration in the environment.



a) b)

Fig. 1. (a) Electrochemical cell where "*1*" – diffusion barrier, "*2*" – locking ring, "*3*" – working electrode, "*4*" – reference electrode, "*5*" – auxiliary electrode, "*6*" – electrolyte, (b) Installation diagram of magnetron sputtering

2.2. Synthesis of electrodes

In our work we use the technology of magnetron sputtering for the deposition of nanocomposite thin film electrodes. Amorphous carbon based material is characterized by unique properties [7] which can be even extended by inserting the metal nanoclusters [8].

In this work, we use amorphous carbon as a material for the electrochemical electrodes, since it is a highly inertial material with good stability in many acids, solvents, and electrolytes. The amorphous matrix provides a reasonable electrical conductivity and the necessary permeability to gas diffusion, while the noble metal nano particles provide higher electrochemical activity as compared to bulk catalysts. The catalyst sensitivity and selectivity can be additionally increased by optimizing the size of the noble metal clusters.

The a-C/Pt thin films are deposited by magnetron co-sputtering of carbon-platinum target in argon. We note here that the platinum target was inserted in the carbon one. The synthesis of a-C/Pt catalyst is conducted on a magnetron facility equipped with the magnetron of constant current and system ensuring the carrier rotation (see Fig. 1b). The films are deposited on a porous polytetrafluoroethylene FM-400 (PTFE) substrate with 15 mm diameter at room temperature. The argon pressure is 10^{-1}–10^{-2} Pa and the magnetron operating conditions are U=500 V, I=200 mA. The thickness of the thin film electrodes was changing and is around 0.4 μm.

a) b) c)

Fig. 2. (a) Pasted electrode and synthesized electrodes: (b) working, (c) reference and auxiliary.

The electrodes fabricated using the pasted powder catalyst (Fig. 2a) and magnetron deposition (Fig. 2b and Fig. 2c) are shown in Fig. 2. The second option is performed in this work. It ensures higher selectivity, increased long-term stability, reduced leakage current and reduced dependency on temperature and pressure.

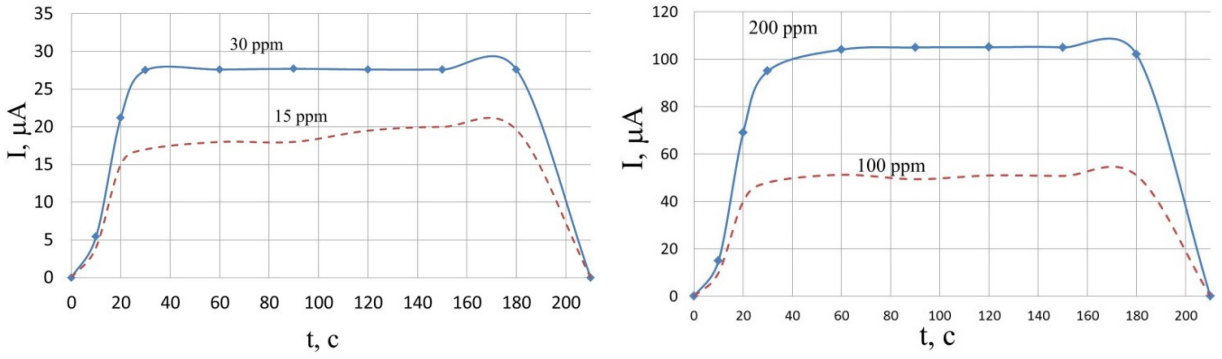
3. Experimental Results

In this section we evaluate the sensor performance in terms of selectivity and response. In fact, we conduct all the experiments for CO and H_2S sensors. The experiments are conducted on ten sensors of each type and, therefore, present average results. The developed thin film electrodes are embedded in the sensor nodes with a liquid electrolyte and tested in the presence of CO and H_2S. The results of this evaluation are presented in Table 1.

Table 1. Cross sensitivity of carbon monoxide and hydrogen sulfide sensors.

Tested Gas	Concentration (ppm)	Sensors' readings (ppm)	
		CO	H_2S
Chlorine (Cl)	100	0	0
Carbon monoxide (CO)	100	100	0
Hydrogen sulfide (H_2S)	30	0.5	30
Nitrogen dioxide (NO_2)	30	0.3	0
Hydrogen chloride (HCl)	100	0	0
Sulfur dioxide (SO_2)	25	0	0
Formaldehyde (CH_2O)	10	0	0
Ethylene oxide (C_2H_4O)	100	0	0
Ammonia (NH_3)	200	0	0

Fig. 3a and Fig. 3b show the sensor response with respect to 15 and 30 ppm H_2S concentrations, as well as 100 and 200 ppm CO. The gases were supplied for three minutes in each experiment. We note that $T_{0,9}$ (time required to achieve 90% of maximal signal response) does not exceed 30 s for all the cases.



a) b)

Fig. 3. Typical response and recovery characteristics to (a) H_2S, (b) CO.

4. Conclusion

In this paper, we have presented electrochemical sensors based on thin film nanocomposite electrodes which are manufactured using magnetron sputtering. Experimental results have shown high potential of magnetron sputtering approach for fabricating the electrodes sensitive to CO and H_2S gases. The developed sensors are selective to toxic gases and have good sensitivity in terms of the response signal.

The results of this work can be used for developing actions to prevent dangerous situations, e.g. gas leaks, fire, and poisoning of the staff.

In the future we intend to develop and evaluate wireless gas sensor nodes with the sensors presented in this work and deploy them in real settings.

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