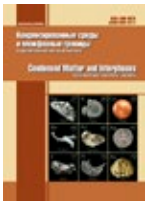

ISSN 1606-867X (Print)
ISSN 2687-0711 (Online)
Condensed Matter and Interphases
Kondensirovannye Sredy i Mezhfaznye Granitsy
https://journals.vsu.ru/kcmf/

Original articles

Research article
https://doi.org/10.17308/kcmf.2023.25/11263

Features of the resistive response to ozone of semiconductor PdO sensors operating in thermomodulation mode

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Abstract

This work is dedicated to the issue of increasing the selectivity of semiconductor PdO sensors in case of ozone detection.

Thin PdO films were obtained using thermal sputtering of Pd and its subsequent oxidation. We characterised the obtained material using X-ray diffraction analysis and optical spectroscopy. We studied the gas-sensing properties of thin films in the mode of periodically changing temperature. The use of the thermal modulation mode allowed discovering the extremes of the resistive response of the PdO sensor in ozone, which helped to increase the selectivity of the sensor while detecting this gas.

We suggested a possible mechanism of ozone chemisorption, which determined the specific form of the thermally modulated PdO response. The studies of the resistive response of PdO sensors under the conditions of ultraviolet illumination confirmed the suggested mechanism of ozone chemisorption.

Keywords: Semiconductor gas sensors, Palladium oxide, Ozone, Thermal modulation mode, Features of resistive response of sensors, Oxygen chemisorption mechanism, Oxygen chemisorption under the conditions of UV illumination

Funding: The study was supported by the Russian Foundation for Basic Research, grant No. 20-03-00901; the Ministry of Education and Science of the Russian Federation in the framework of the state order to higher education institutions in the sphere of scientific research for years 2020–2022, project No. FZGU-2020-0036; the Ministry of Education and Science of the Russian Federation, agreement No. 075-15-2021-1351, regarding automation of electrophysical measurements.

For citation: Ryabtsev S. V., Obvintseva N. Yu., Chistyakov V. V., Al-Habeeb A. A. K., Shaposhnik A. V., Turishchev S. Yu., Domashevskaya E. P. Features of the resistive response to ozone of semiconductor PdO sensors operating in thermomodulation mode. *Condensed Matter and Interphases*. 2023;25(3): 392–397. https://doi.org/10.17308/kcmf.2023.25/11263

Для цитирования: Рябцев С. В., Обвинцева Н. Ю., Чистяков В. В., Аль-Хабиб А. А. К., Шапошник А. В., Турищев С. Ю., Домашевская Э. П. Особенности резистивного отклика на озон полупроводниковых сенсоров PdO, работающих в режиме термомодуляции. *Конденсированные среды и межфазные границы*. 2023;25(3): 392–397. https://doi.org/10.17308/kcmf.2023.25/11263

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1. Introduction

The analysis of gas media is required in order to ensure safety in production, to control various technological processes, in environmental monitoring, scientific research, healthcare, etc. We believe that the devices based on semiconductor gas sensors (SCGS) may be the most suitable for these purposes. As compared to other gas analysers, their advantages include the low cost of manufacture, energy efficiency, high sensitivity, a lack of need for consumable products in the gas analysis process, and analysis continuity. The idea of their operation is changing the resistance of the oxide semiconductor material in the medium of a particular gas due to chemisorption. SCGS also have some disadvantages, among which is low selectivity in the detection of gas mixtures. There are several ways to neutralise this disadvantage, for example, by creating multi-sensor systems that consist of partially selective sensor elements. Signals from this array of sensors are processed using artificial neural networks, the principal component analysis, etc. Another known method of increasing selectivity is by modulating the operating temperature of sensors [1–4]. The sensor temperature can be changed according to a sinusoidal law or it may have another periodic form [5]. The informative value of the resistive response of the sensor in this mode of operation is significantly improved due to several reasons. The law of transformation of the gas adsorption effect into the resistive response of the sensor is of non-linear nature [1–4]. Therefore, the temperature-modulated resistive response may have typical features in the form of harmonics, the amplitude-frequency characteristics of which are discovered by the Fourier transformation of the sensor signal [1–5]. A change in the sensor temperature also leads to a shift in the adsorption-desorption equilibrium, which, in its turn, causes the formation of different charge states of particles on the sensor surface. For instance, the charge states of chemisorbed oxygen change in this way on the sensor surface in the course of heating or cooling [6]. This process is rather specific for each adsorbent-adsorbate pair and has an effect on the shape of the resistive response of the sensor. The problem of selectivity can be solved to some extent using the analysis of the sensor response forms in the course of thermal modulation.

The goal of this work was to identify the features and mechanisms of formation of the resistive response of sensors in the presence of ozone, which can ensure its selective detection. In this work we used semiconductor PdO films operating in the thermal modulation mode were used as sensors.

The research is relevant, on the one hand, due to by the widespread use of ozone in various technological processes, and on the other hand, due to its extreme toxicity (first hazard class) and the need for reliable control of the fact that ozone concentration must be controlled in the workplace.

2. Experiment

We used ~30 nm thick PdO films and determined their thickness using an LEF-757 ellipsometer. We obtained oxide films using air oxidation of metallic Pd layers deposited on dielectric substrates by thermal evaporation at a temperature of 550 °C. The dielectric substrates had platinum electrodes for measuring film resistance and a platinum heater which also served as a temperature sensor.

According to X-ray diffraction analysis, the obtained layers had a tetragonal structure (Fig. 1).

Using spectroscopic studies in the range of 300-900 nm (4.1–1.4 eV), we determined the band gap of PdO. Plotting the spectroscopic data in Tauc coordinates resulted in value E_g ~ 2.3 eV (Fig. 2).

The semiconductor nature of the conductivity of the obtained oxide layers was also confirmed by gas-sensor experiments. In the course of chemisorption of ozone (an electron acceptor gas), the resistance of PdO sensors decreased, which corresponded to the *p*-type semiconductor conductivity.

In the thermal modulation mode, the temperature of the PdO sensor varied from 50 to 300 °C according to a sinusoidal law with a period of 256 seconds. Over the course of the experiments, we recorded the current resistance of the sensors at a frequency of 16 measurements per second.

The sensors were tested in clean air and with an ozone concentration in the air of 250 ppb (1 ppb is 10^{-7} volume %) using a GS-024-25 ozone generator. The ozone generator included

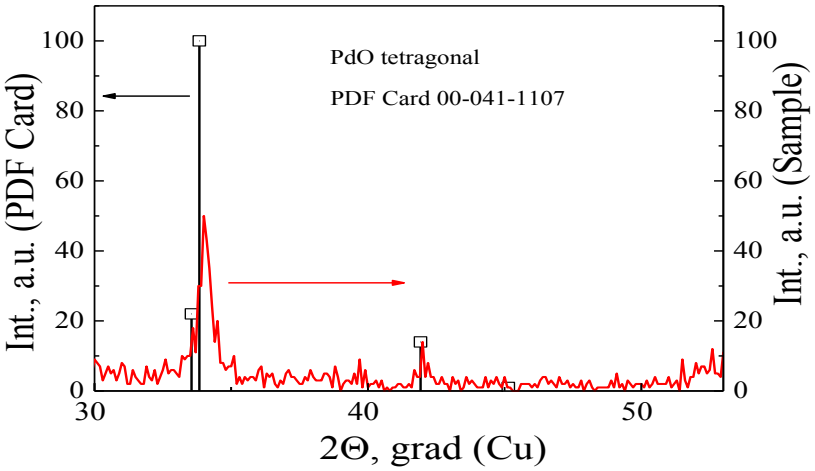

Fig. 1. The diffraction pattern of a PdO film

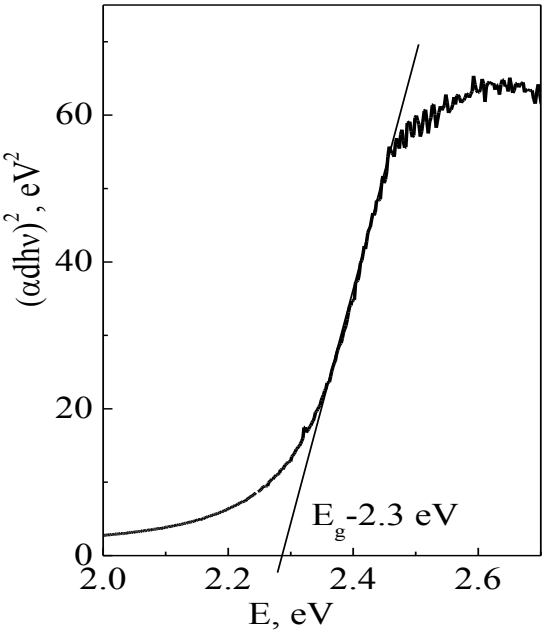

Fig. 2. Optical spectrum near the absorption edge of a thin PdO film

a special filter which lowered the background concentration of ozone that is always present in ordinary air to zero.

3. Results and discussion

Figure 3 shows the results of the experiment obtained using a thin-film PdO sensor operating in the thermal modulation mode of 50–300 °C. We are going to compare the resistive response of the sensor in clean air (the black curve) and in air with 250 ppb ozone (the blue curve).

After replacing the air in the measuring cell with an air-ozone mixture, transformation processes were observed for ~1 hour and included a change in the signal amplitude, its shape, and a signal shift along the resistance scale. Figure 3 shows the data for three periods of 256 seconds each, which were obtained after determining stationary values of the resistive response in air and in an air-ozone mixture.

The resistive response of the sensor with 250 ppb ozone was lower than the response in clean air, as ozone has a higher affinity to the electron than oxygen in the air. In the course of ozone chemisorption, an additional part of electrons was localised at its levels. For a *p*-type semiconductor, this resulted in a decrease in its resistance (Fig. 3.)

The shape of the signals is primarily determined by the dependence of the resistance of the semiconductor on its temperature (the resistance decreases for non-degenerate semiconductors with increasing temperature, since the concentration of charge carriers grows). Therefore, in vacuum or inert gases with sinusoidal thermal modulation, a resistive response of the sensor of the similar shape but antibatic in value should be observed.

In the presence of chemically active gases (air oxygen and ozone), the thermal signal of the sensor changed. This was due to the dependence of the adsorption-desorption equilibrium on temperature. Differences in the forms of signals (Fig. 3) from a purely "thermal sinusoid" were associated with this factor. The signal shape was specific for each adsorbent-adsorbate pair, as it was shown in our previous works [7, 8]. The

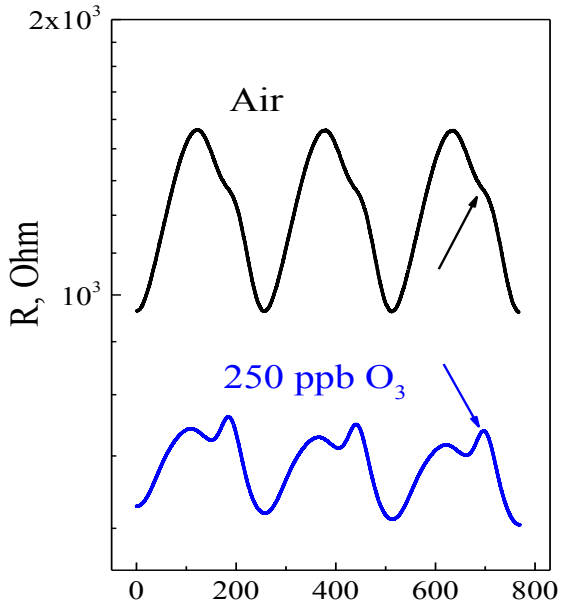

Fig. 3. Resistive response of a PdO sensor in thermal modulation mode in clean air and in air with 250 ppb ozone

resistive response of the PdO-O_3 pair among other oxides and gases that we studied [7, 8] had the greatest differences, which can be used to solve the issue of SCGS selectivity in ozone detection.

We will consider possible chemisorption forms of oxygen and ozone.

It is assumed that within the temperature range of 50–200 °C oxygen is chemisorbed in the molecular form O_2^-, at 150–450 °C in the atomic form O^-, and at >400 °C in the form of O^{2-} [5]. The temperature ranges of oxygen chemisorption in different charge states are rather conventional and differ in the existing literature.

Chemisorption of ozone on the sensor surface occurred in two forms: in molecular O_3^- and in atomic O^- [5]. The charge form O_3^- was unlikely or short-lived due to the fact that ozone rather quickly passed into a less active state on catalytically active surfaces.

Based on the above-studied chemisorption forms, it can be concluded that O^- form is common for both oxygen and ozone. Presumably, this form of chemisorption also determines the features of the plots marked with arrows (Fig. 3). The mentioned features of the air and ozone plots coincided regarding the time of the temperature rate and, as a result, regarding the temperature. In an ozone-containing media, the amount of O^- chemisorbed on the sensor surface increased as compared to air, which could explain the more pronounced feature in the ozone plot (the blue curve).

This mechanism can be confirmed by the experiments with the illumination of sensors using UV radiation with photon energy exceeding the PdO band gap energy (Figs. 4a, b).

An LED with a wavelength of 260 nm (4.8 eV) and an optical power of ~30 mW was used in the experiments. This illumination led to the generation of superequilibrium electron-hole pairs as follows:

$$h\nu \rightarrow e^- + h^+. \quad (1)$$

As a result of photoexcitation, the resistance of the PdO film should naturally decrease in vacuum or in an inert gas due to the appearance of additional charge carriers. However, in other gaseous media, the interaction between superequilibrium charge carriers and particles chemisorbed on the semiconductor surface must be taken into account.

In a medium that contains oxygen or ozone, a negative charge was localised on the surface of the semiconductor, associated with the chemisorption of oxygen in the form O^-, which resulted in surface bending of the semiconductor bands. A positive charge in the form of holes drifted towards it in order to compensate for the surface negative charge. Electrons, on the contrary, drifted into the bulk of the semiconductor, and the ionisation (chemisorption) of oxygen as follows:

$$O_{2(surf)} + 2e^- \rightarrow 2O^-_{(surf)} \quad (2)$$

was impeded [6,9,10]. Still, the holes easily interacted with the already chemisorbed oxygen, which was desorbed from the surface as a result of the reaction:

$$2O^-_{(surf)} + 2h^+ \rightarrow O_2\uparrow \quad (3).$$

In this case, the bending of the bands decreased until an equilibrium was reached between reaction (3) and (2) [6, 9, 10]. In accordance with this model, the resistance of the sensor in air (Fig. 4a) and in ozone (Fig. 4b) under UV illumination was higher than in the dark, as on the whole photodesorption of O^- from the sensor surface according to reaction (3) prevailed.

In order to substantiate our chemisorption model, we should also note that under UV

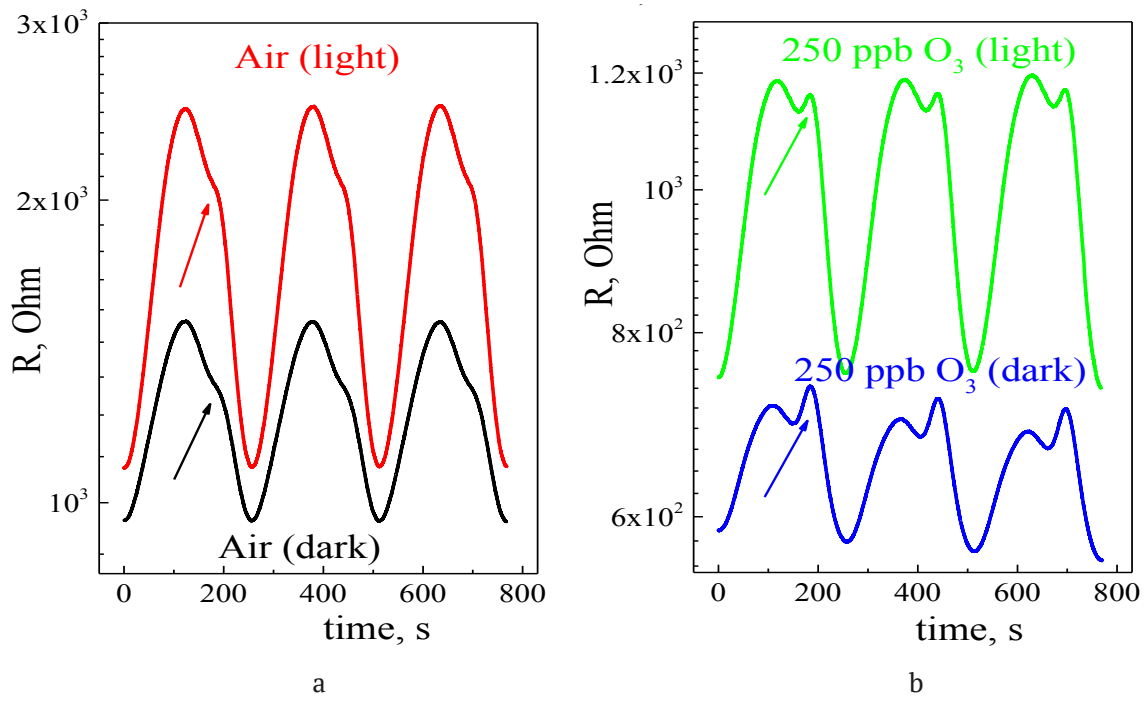

Fig. 4. a) Resistive response of the sensor in air in the dark and under UV illumination; b) Resistive response of the sensor in air-ozone media in the dark and under UV illumination

illumination, the peak on the ozone curve indicated by the arrow (Fig. 4b) decreased. As it was assumed above, this was associated with chemisorbed oxygen in the form of O^-.

4. Conclusions

We studied the resistive response of PdO sensors in an ozone-air mixture in the thermal modulation mode. We discovered specific forms of the resistive response of PdO sensors in the presence of ozone, which can be used to solve the issue of its selective detection.

Possible mechanisms of oxygen and ozone chemisorption were studied. As a result of the analysis of data obtained in pure air and 250 ppb ozone, we assumed that the features of the resistive response of the PdO sensor in both gaseous media were determined using the chemisorption of oxygen in the form of atomic O^- ions.

The results of studying the resistive response of the PdO sensor under UV illumination with photon energies exceeding the band gap of PdO were consistent with the suggested chemisorption mechanism.

Contribution of the authors

The authors contributed equally to this article.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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Received 29.12.2022; approved after reviewing 10.01.2023; accepted for publication 11.01.2023; published online 25.09.2023.

Translated by Marina Strepetova