Structural and gas-sensitive characteristics of thin semiconductor PdO films of various thicknesses during ozone detection

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PdO films were obtained by thermal deposition of palladium metal with a thickness of 30 and 90 nm, followed by its oxidation in air at different temperatures. PdO oxide films are characterized by transmission electron microscopy (TEM) and reflection high-energy electron diffraction (RHEED). Data on the semiconductor properties and gas sensitivity to different concentrations of ozone in the air are obtained. The optimal temperature conditions for the oxidation of the films are established, which ensure their uniform phase composition and the absence of electrical noise during the detection of gases. The mechanism of the electrical noise appearance in ultrathin films associated with their fragmentation during oxidative annealing is proposed and justified. The possibility of detecting ozone impurities in the air below the maximum permissible concentration (MPC) by PdO semiconductor films is shown.

Keywords: palladium oxide thin films, phase composition, electrical noise, gas sensor properties.

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1. Introduction

Recently, ozone is wide spread for technological purposes, for example, decontamination of water in water pipes, pools, aquaparks, discharge treatment, paper whitening, etc. As ozone is an unstable gas, it is usually produced by special generators directly in a place of its usage. At the same time, ozone is one of the most toxic gases. The maximum permissible concentration (MPC) of ozone in air in a working area is 0.1 mg/m^3 or $\sim$ 50 ppb (1 ppb — 10^{-7} vol%). That is why safety in stations of production and application of ozone is ensured by continuous and multi-point monitoring of its content in an ambient air. Mostly, this task is solved by instruments based on an optical principle of detection. These instruments have a number of disadvantages: high cost and power consumption, and it is also difficult to maintain them. Furthermore, they are designed to analyze ozone only in one point of location of the optical sensor. An alternative includes instruments based on semiconductor sensors of the resistive type [1]. The main advantages of the sensor instruments include absence of consumables, a possibility of multi-point and continuous monitoring of the air in the working area. Sensors of these instruments are based on semiconductor oxides. The sensor characteristics are largely determined by selection of a material of a gas-sensitive layer as well as its production technology. The sol-gel technology is most often used and it provides for formation of a highly-developed surface, which is the most accessible for gas adsorption. The present paper discusses a thin-film technology of deposition of gas-sensitive layers, as it is well combined with well-tested microelectronics technologies, thereby providing substantial reduction of cost the gas control analytical instruments.

Most often, ozone is detected by applying the WO_3, In_2O_3, SnO_2, ZnO oxides, both individual and those with various additives. The present paper applies a new sensor oxide material PdO, which has been offered for the first time to analyze ozone in our previous papers [2–5].

The present study is aimed at establishing the gas-sensitive properties of thin PdO films of various thicknesses and optimizing their production technology so as to detect the ozone concentrations below the MPC level.

2. Experimental part

The PdO films were produced by thermal deposition of metal Pd to various substrates with their subsequent oxidation in air. The optical studies were carried out by using glass plates, while the studies of the transmission electron microscope (TEM) were carried out on the substrate of monocrystalline KCl with a sublayer of amorphous carbon.

The metal Pd was deposited to the substrates at the rate of $\sim$ 1 nm/min.The Pd deposition rate was determined when studying a cross chipped face of the films based on the monocrystalline silicon substrate using the scanning electron microscope. The thicknesses of the working samples were calculated to be 30 and 90 nm. The produced metal films were annealed in the air atmosphere for 1 h at the temperatures 240, 400 and 600°C. They were characterized thereafter.

The optical studies of the transmission spectra were carried out on the Ocean Optics fiber-optic spectrometer. The phase composition and the microstructure of the films were investigated by the reflection high-energy electron diffraction (RHEED) and microscopy on the Karl Zeiss Libra 120 TEM. The electrophysical and gas sensor properties of the films were investigated on special multi-core substrates (Al_2O_3) with incorporated Pt electrodes for measurement of the film resistance. A Pt heater meander was applied to another side of the substrates so as to be a temperature sensor at the same time. In the experiments, the sensor temperature was maintained with the accuracy of 1°C.

The different concentrations of ozone in air were obtained by means of the ozone generator GS-024-25 (JSC „OPTEK").

3. Results and discussion

3.1. Band gap and structural characteristics of the PdO thin films of a various thicknesses

As it is specified in the reference data, PdO is a semiconductor oxide of the *p*-type with the band gap of 2.2–2.7 eV [6–8]. A semiconductor character of the films studied in the present paper is confirmed by optical spectroscopy methods. The transmission spectra of the PdO films are of a kind that is typical for semiconductor materials — with sharp transmission decrease near the fundamental electron transition band–band $E_v - E_c$. The Tauc coordinates $E - (\alpha d h\nu)^2$ had been used to determine the band gap of the PdO films E_g (Fig. 1). The straight lines drawn to straight sections of the optical spectra to the abscissa axis are extrapolated to give the values of $E_g = 2.27$ eV and $E_g = 2.21$ eV (Fig. 1) for the PdO films of the thickness ~ 30 and ~ 90 nm, respectively. The obtained values E_g full comply with the known reference data for this oxide [6–8].

Both the metal Pd films were oxidized in the same conditions at 550°C for 1 h. Small differences of the values E_g are associated to film thicknesses. We suppose that the thicker film has more defects than a thin one. That is why tails of localized states in the gap have a bigger density, thereby somewhat reducing a graphically calculated value E_g.

Figures 2 and 3 show the electron diffraction patterns and TEM-images of the Pd film at various oxidation stages thereof. The electron diffraction patterns were analyzed to show that the initial films (see Fig. 2, *a*, and 3, *a*) are metal palladium without visible traces of oxide phases. The same phase composition is in the films, which are annealed in the air atmosphere at 240°C (PDF card 00-041-1043 [9]).

Further increase in the annealing temperature of the Pd films in the air atmosphere at 400 and 600°C results in formation of the tetragonal oxide PdO phase (PDF card 00-041-1107 [9]). At these annealing temperatures, the phase of the metal palladium in the films can not be detected by the RHEED, i.e. the palladium oxidation process is fully completed and the film acquires a single-phase composition of the tetragonal PdO.

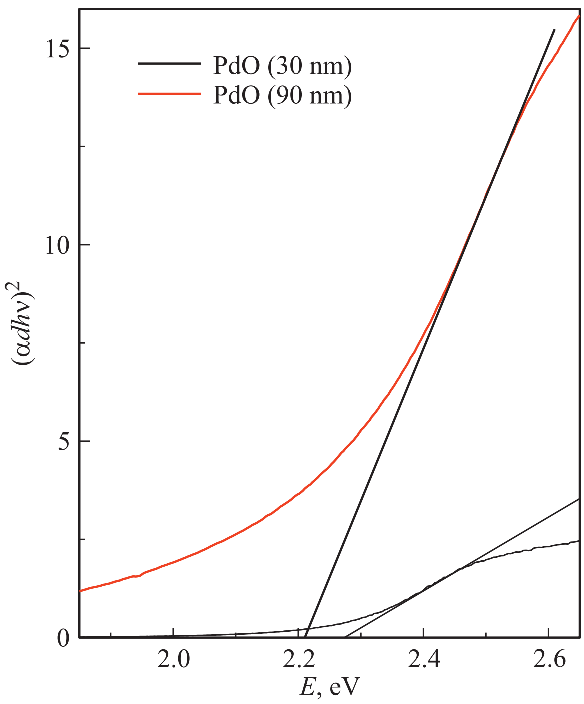

Figure 1. Optical spectra of the PdO films of the thickness 30 and 90 nm in the Tauc coordinates.

One of the features of oxidation annealing in the thin film of the thickness of 30 nm is coarsening of crystallites during annealing both in the Pd film (Fig. 2, *b*), and in the PdO films (Fig. 2, *c* and *d*). In doing so, the films are losing their initially solid structure. The growth of the crystallite sizes and formation of film gaps are proportional to increase in the annealing temperature. Such aggregative recrystallization substantially affects electrophysical properties of the films. The oxidation annealing of the films applied to the test structures included recording their existing resistance, which was monotonically increasing with the increase in the temperature. It is mostly associated to oxidation of the metal palladium to the semiconductor oxide of higher resistance.

An important aspect during annealing was emergence of electrical noise at the temperatures > 550°C, which is directly associated fragmentation of the thin films if judging by data of the microscope studies (Fig. 2). We suppose that progressing fragmentation of the film deteriorates the quality of contacts between the crystallites, thereby causing the electrical noise. Above 600°C, there is a sharp decrease in the noise level, as well as the film resistance. At the temperature 650–700°C, the fragmentation of the films is completed, thereby resulting in full disappearance of the electrical conductivity of the films.

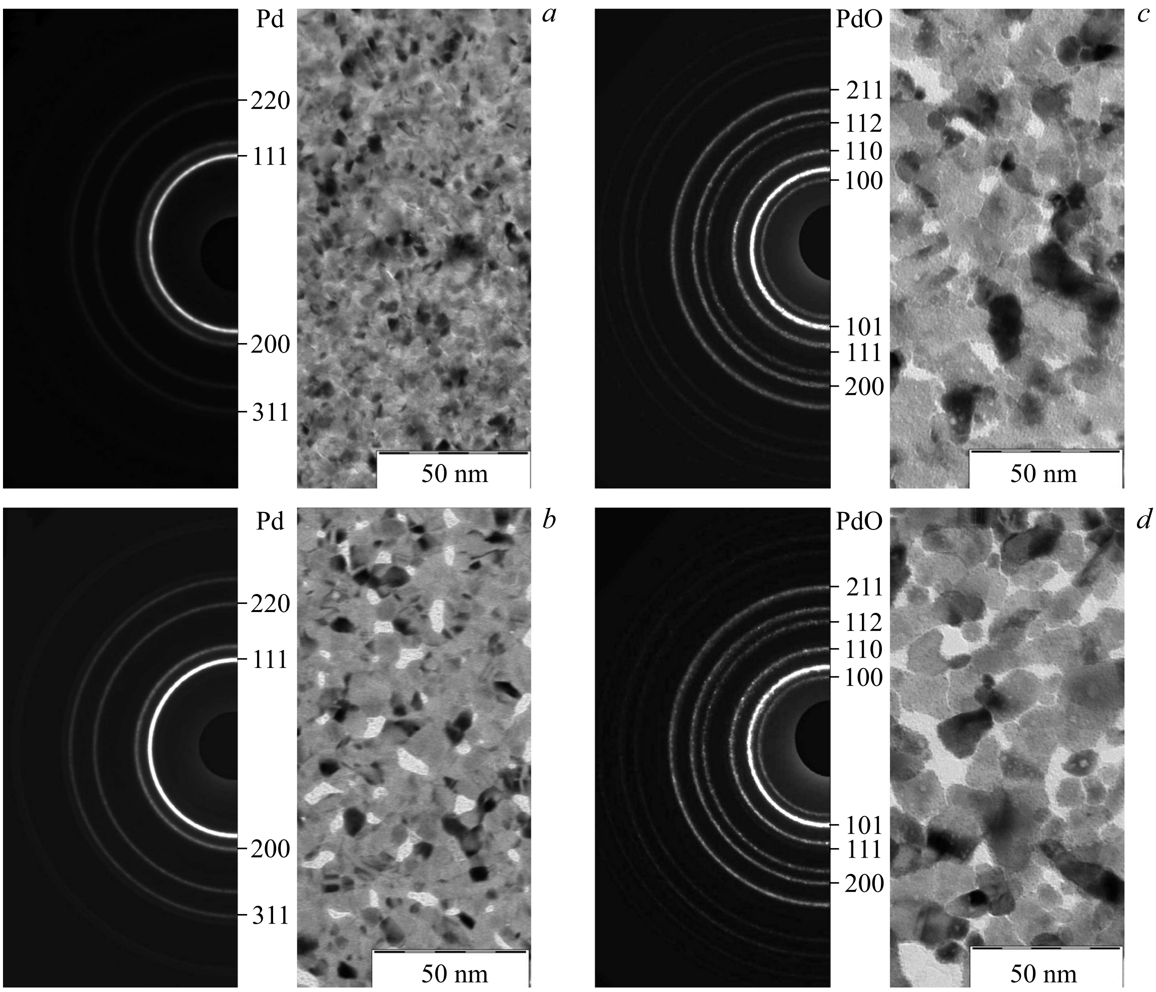

Figure 2. Electron diffraction patterns and TEM-images of the Pd initial film of ~ 30 nm (a) and the films annealed at the temperatures 240 (b), 400 (c) and 600°C (d).

Thus, for the PdO films of the thickness of 30 nm, the optimum annealing temperature should not exceed 550°C, thereby, on the one hand, ensuring the single-phase composition of the films, while, on the other hand, — no electrical noise to prevent accurate resistance measurements.

Fig. 3 shows the electron diffraction patterns and TEM-images of the thicker initial Pd film of the thickness of 90 nm and the same films annealed in the air at the temperatures 240, 400 and 600°C. Regularities correlated to fragmentation of the PdO films remain in this case, too, but they are less pronounced. After oxidation annealing, the films exhibit some discontinuous areas. With increase in the annealing temperatures, there is also evident coarsening of the microcrystallites. These films differ from the above-discussed ones in that the electrical conductivity noise is observed at higher temperature of the oxidation annealing > 650°C.

Conductivity of *p*-type for the PdO films had been previously established by us when studying the Seebeck effect for the thin-film samples [4]. This fact is also confirmed by a character of the resistance response of the PdO films in the ozone medium — an oxidizer gas (Fig. 4). As it is expected for the semiconductor *p*-type, the resistance of the PdO films decreased in the oxidation medium of ozone (Fig. 4), which correspond to known mechanisms of the sensor response [10].

3.2. Gas-sensitive properties of the PdO films of various thicknesses

The gas-sensitive properties of the PdO films were studied at various concentrations of ozone 25, 55, 90 and 250 ppb in the air. The films studied in the present paper have various resistance values. That is why for correct comparison of their sensor properties it is necessary to represent data in relative units $\Delta R/R_0$, where ΔR — the difference of resistance values of the sensor in the air and the ozone-containing medium R_0 — resistance of the films in clean air. In the experiments of ozone detection, the operating temperature of the PdO films was 150°C. The resistance response of the PdO films of the various thicknesses of 30 and 90 nm is shown on Fig. 4.

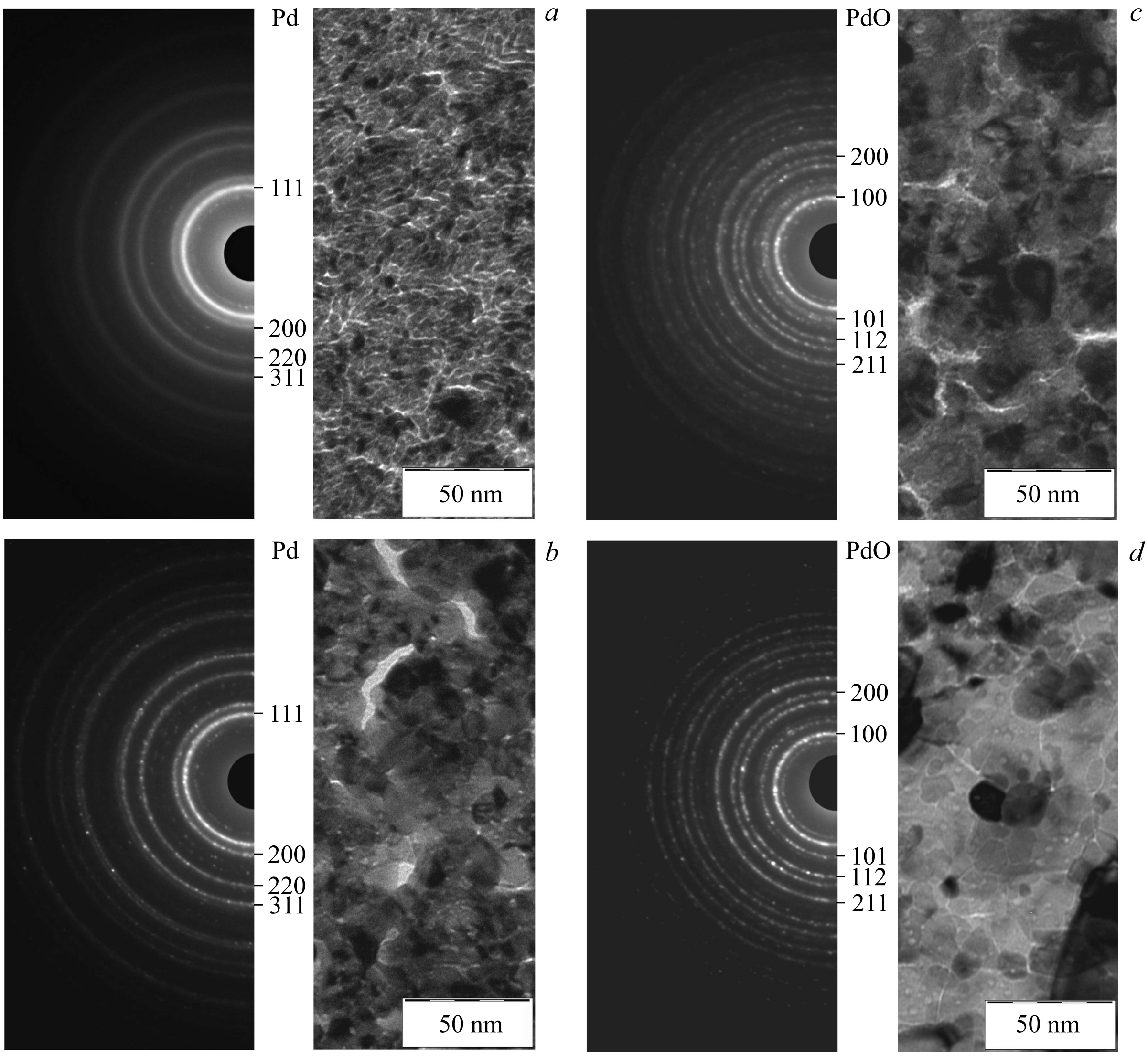

Figure 3. Electron diffraction patterns and TEM-images of the Pd initial film of $\sim$ 90 nm (*a*) and the films annealed at the temperatures 240 (*b*), 400 (*c*) and 600°C (*d*).

The resistance response in the PdO films of the various thicknesses is compared on Fig. 4 to show that the thicker film has a lower response within the high concentrations of ozone and somewhat worse kinetics of the sensor signal relaxation after blowing a measurement cell with air without ozone impurities. Furthermore, the resistance response of the PdO film (90 nm) has lesser steepness (Fig. 5), thereby worsening the accuracy of quantitative analysis of ozone within a wide range of concentrations. The results indicate a lower adsorption capacity of the sensor in relation to ozone, because the bulk regions of the thicker layer are inaccessible for chemisorption and shut the change of the electrical conductivity of the surface areas and, therefore, weaken the sensor effect. That is why the thicker films exhibit faster saturation of the adsorption capacity and they have a lesser resistance response at relatively high concentrations of gases.

On the other hand, the curves $\Delta R/R_0 - C$ (see Fig. 5) are extrapolated towards small concentrations to show an advantage of the thicker film in a value of the resistance response at the concentrations of ozone < 25 ppb.

Thus, the revealed features of the sensor properties of the PdO films of the various thicknesses allow establishing areas of their predominant application by the concentration of ozone in the air. Note that the sensors with high sensitivity to ozone of low concentrations (in ppb) are required in scientific research [11], including for monitoring the background content of ozone on the clean atmosphere air. The analysis of ozone within the wide range of concentrations is required for technological purposes and to ensure production safety.

The reference data was analyzed to show that minimum concentrations of ozone, which are determined by means of the semiconductor sensors, range from several to dozens

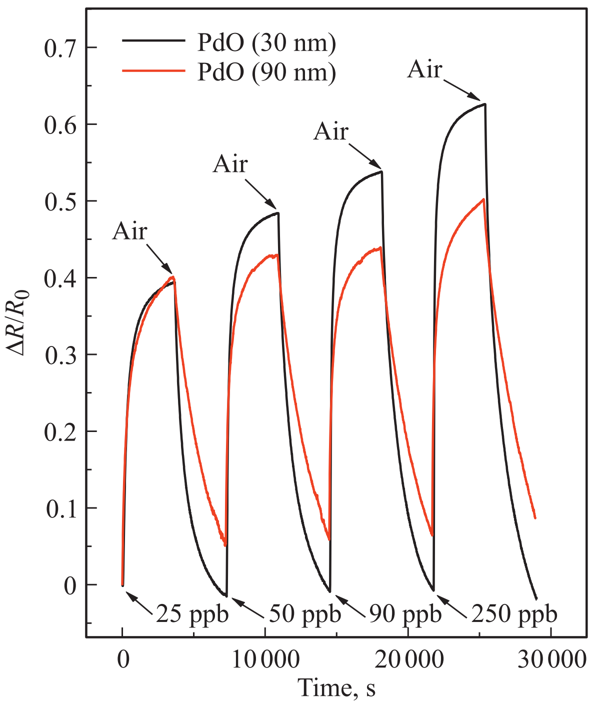

Figure 4. Resistance response of the PdO films of the thickness of 30 and 90 m in relative units for various concentrations of ozone in the air.

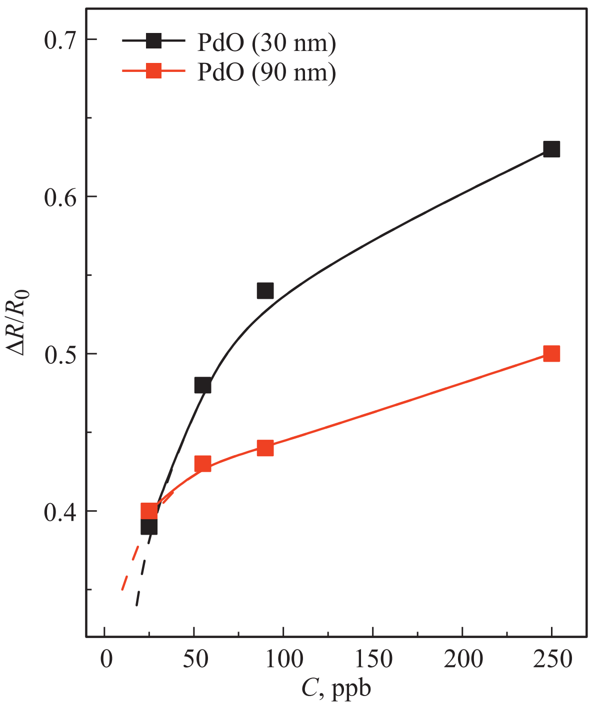

Figure 5. Dependence of the maximum value of relative response of the PdO films of the thickness of 30 and 90 nm on the concentration of ozone in the air.

of ppb [11–15]. The results obtained in the present paper correspond to these reference data. The PdO sensor layers produced by the above-described technology allow detecting ozone in the air, when it is substantially lower the maximum permissible concentration in the working area.

4. Conclusion

The ultrathin semiconductor PdO films are produced to detect ozone in air by thermal oxidation of the metal palladium layers and their subsequent oxidation in the air. The optimum temperature of oxidation annealing of the sensor layers is around 550°C, thereby ensuring their single-phase composition and not leading to the critical fragmentation of the films.

The fragmentation of the PdO films in increase in the oxidation annealing temperature, which is established by the TEM method, results in emergence of electrical noise during resistance measurements.

The PdO of the various thicknesses (30 and 90 nm) have various gas-sensitive properties and can be applied to detect ozone both in the wide concentration region (30 nm), and in the region of low concentrations of ozone (90 nm), when it is substantially lower than 25 ppb.

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Conflict of interest

The authors declare that they have no conflict of interest.

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