ISSN 0012-5016, Doklady Physical Chemistry, 2016, Vol. 470, Part 2, pp. 158–161. © Pleiades Publishing, Ltd., 2016.
Original Russian Text © S.V. Ryabtsev, A.V. Shaposhnik, A.M. Samoylov, A.A. Sinelnikov, S.A. Soldatenko, S.B. Kuschev, V.M. Ievlev, 2016, published in Doklady Akademii Nauk, 2016, Vol. 470, No. 5, pp. 550–553.

PHYSICAL CHEMISTRY

Thin Films of Palladium Oxide for Gas Sensors

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Received February 1, 2016

Abstract—Thin films of PdO obtained by thermal oxidation of Pd films in air in the temperature range of 240–800°C were characterized using fast electron diffraction, transmission electron microscopy, and optical spectroscopy. The PdO films were found to be non-stoichiometric. With increasing oxidation temperature, the deviation of the PdO film composition from the stoichiometric component ratio becomes less pronounced. The resistivity response of PdO films to the presence of ozone in air was studied for the first time and good prospects for using this material for gas sensors are demonstrated.

DOI: 10.1134/S0012501616100055

Ultradispersed Pd/PdO particles present on the surface or in the bulk of SnO_2 and ZnO oxides are known to activate their gas sensitivity [1, 2]. Examination of published data showed the absence of papers considering the gas sensitivity of PdO films as a self-sufficient semiconductor sensor material.

The purpose of this study is to synthesize palladium oxide thin films and to characterize them by transmission electron microscopy (TEM) and optical spectroscopy and also to investigate their gas-sensitive properties for the detection of oxidizing gases.

EXPERIMENTAL

Synthesis of PdO Films and Investigation Methods

The initial ~30 nm thick palladium films were obtained by thermal sublimation and condensation of the metal in vacuum with deposition on non-heated subsrates. For measuring the electrical parameters, the Pd films were formed on polished polycrystalline Al_2O_3 plates. The optical properties were studied for films deposited on quartz plates. Films for TEM measurements were formed on Si substrates with a buffer SiO_2 layer and on KCl substrates with an amorphous carbon layer. The Pd film thickness was specified by selecting the metal condensation time at a condensation rate of ~0.016 nm/s. The Pd films were oxidized by annealing in air at T_{ann} = 240, 300, 400, 550, 600, and 800°C for 1 h.

The phase composition and substructure of the films were measured by fast electron diffraction (FAD) and transmission electron microscopy (TEM) on EMV-100 BR and Karl Zeiss Libra 120 electron microscopes. The electron diffraction patterns were interpreted using the JCPDS database [3].

The electrical properties and gas sensitivity of PdO films on test alumina substrates (Al_2O_3, 2 × 3 mm) with platinum electrodes were measured on a Hioki 3522-50 instrument. The optical properties of the PdO films synthesized at different temperatures were investigated on a Shimadzu UV-210A double-beam spectrophotometer.

RESULTS AND DISCUSSION

Phase composition, structure, and orientation of the films. According to FAD data, the initial single-phase Pd thin films have a highly dispersed polycrystalline structure with arbitrary grain orientation, grain size varying from 0.5 to 6 nm. The cubic unit cell parameter of Pd films is a = 0.3912 ± 0.0002 nm, which exceeds the reference values by 0.6% [3].

Since Pd was vaporized by sublimation and the condensation rate was rather low (~0.016 nm/s), the change in the unit cell parameter is, presumably, a consequence of hydrogen atom absorption [4].

It was found by FAD that annealing of Pd films in air at temperatures below 300°C does not induce

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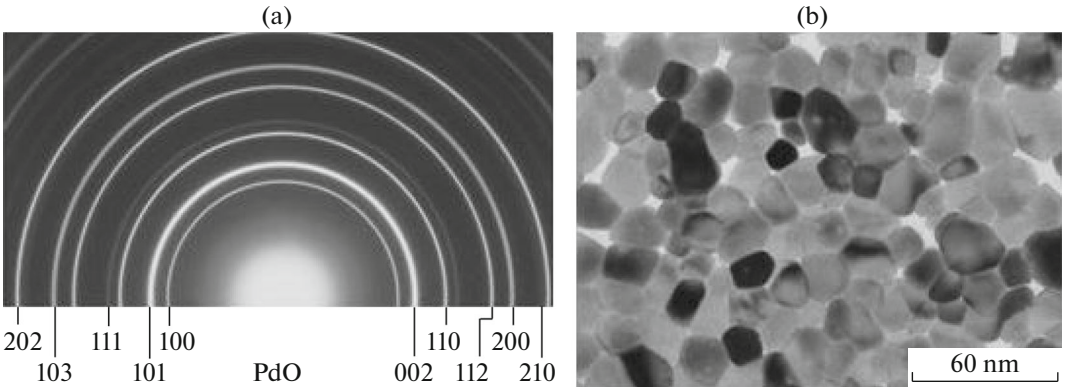

Fig. 1. (a) Electron-diffraction pattern and (b) light-field TEM image of PdO films obtained by annealing in air at $T_{ann} = 600°C$.

changes in the phase composition, which is indicative of insufficient activation towards oxidation. When $T_{ann} = 300°C$, partial oxidation takes place to give two-phase films: apart from Pd, palladium oxide PdO is detected (tetragonal crystal lattice, $a = 0.3043 \pm 0.0002$ nm and $c = 0.5337 \pm 0.0002$ nm) [3]. In the electron diffraction patterns of these samples, the relatively high intensity of the (100) ring, which is forbidden for the PdO space group $P4n2$, implies that the oxide is non-stoichiometric [5]. The average grain size of each phase is about 8 nm. In two-phase samples, the palladium unit cell parameter corresponds to the reference value, which means that hydrogen atoms have escaped from Pd on heating.

Raising the annealing temperature to 500°C resulted in the formation of single-phase PdO films. On further increase in T_{ann} from 600 to 800°C, the phase composition did not change and only the average grain size increased to ~15 nm (Fig. 1).

Optical absorption spectra. We present the primary transmission spectra of the samples (Fig. 2a) and the spectra plotted in the $(\alpha dh\nu)^2-E$ coordinates (Fig. 2b). From Fig. 2a (spectrum *1*), it follows that the Pd films annealed at 240°C for 1 h have a low transmission coefficient $T = f(\lambda)$, typical of metals, over the whole wavelength range. The structured spectrum characteristic of semiconductors is recorded for samples oxidized above 300°C, which is in good agreement with the phase composition data. For samples oxidized at $T_{ann} = 300$, 400, or 550°C (Fig. 2a, spectra *2–4*), the transmission coefficient in the wavelength range above 500 nm monotonically increases with increasing the annealing temperature, indicating an increase in the fraction of the semiconductor phase, i.e., PdO. A minimum change in the transmission coefficient of the films was found as the annealing temperature increased from 600 to 800°C, indicating a semiconductor nature of the conduction of the whole bulk of films oxidized at these temperatures.

The bandgap of ultrathin films resulting from Pd oxidation calculated by the graphical method monotonically increases, being $\Delta E_g = 2.15$, 2.2, 2.25, and 2.3 eV for $T_{ann} = 400$, 550, 600, and 800°C, respectively. The results support the known published data about the semiconductor properties of PdO films with *p*-type conduction and bandgap ΔE_g of ~2.2–2.7 eV [6–9].

A possible cause of the increase in the bandgap is the presence of density-of-states tails in the semiconductor bandgap, which is typical of samples with a composition deviating from the stoichiometric component ratio. The bandgap $\Delta E_g = 2.3$ eV corresponds to PdO samples with minimum non-stoichiometry. The obtained results are in line with the capacitance–voltage characteristics of PdO films on silicon [10].

Gas sensitivity of PdO films. In *p*-type semiconductors, chemisorption of gases with a high electron affinity results in enrichment of the near-surface region with the major charge carriers. The electrical conductivity of the film thus increases. Electrical conductivity measurements upon chemisorption of the reducing and oxidizing gases, for example, hydrogen and oxygen, make it possible to determine the type of conduction of the semiconductor. In sensor experiments, ozone was used as a highly potent oxidant. The investigation was carried out on test structures with PdO films synthesized at 600°C. The resistivity response of PdO films measured at 220°C is shown in Fig. 3. The reproducibility of the response of the sensing structure based on PdO thin films was confirmed by repeated cycles of measurements with the same ozone concentrations in air (0.5, 0.32, 0.19, and 0 mg/m^3).

The varioation pattern of the resistivity response to the presence of ozone in air corresponds to the previously established *p*-type of conduction of palladium oxide. The data (Fig. 3) on the magnitude, reproducibility, and kinetics of the resistivity response (the experimental points in the plots were measured every

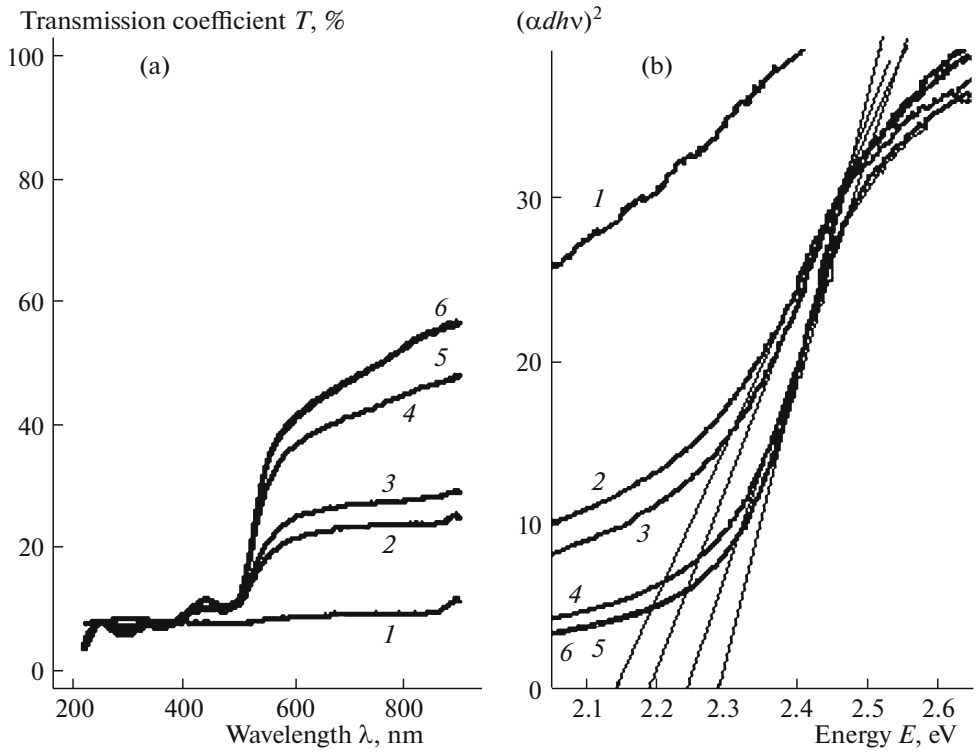

Fig. 2. Transmission spectra of films after annealing for 1 h at various temperatures (°C): (*1*) 240, (*2*) 300, (*3*) 400, (*4*) 550, (*5*) 600, (*6*) 800. (a) Transmission coefficient plotted vs. the wavelength; (b) $(\alpha dh\nu)^2$ plotted vs. the photon energy.

10 s) attest to high efficiency of PdO thin films as sensing materials as compared with other materials used to detect oxidizing gases [11–13].

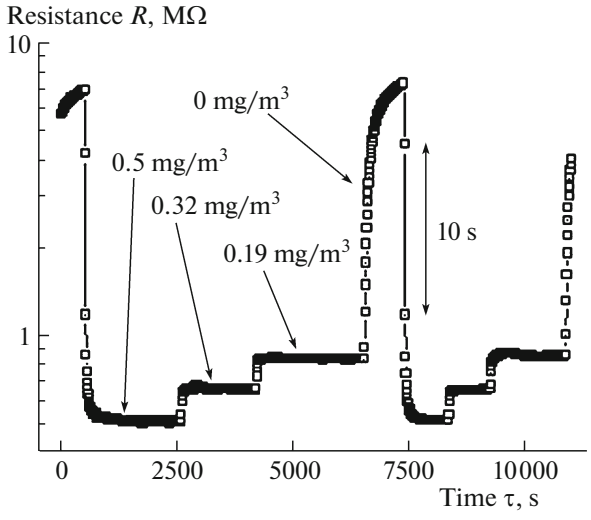

Fig. 3. Variation of the PdO film resistance with time for various ozone concentrations in air.

CONCLUSIONS

The possibility of synthesizing PdO thin films by thermal oxidation of Pd films in air at temperatures of 500–800°C was demonstrated by FAD, TEM, and optical spectroscopy methods.

The resistivity response of PdO thin films to the presence of ozone in air was detected for the first time. The magnitude of the response attests to good prospects for using this material in the design of sensors for detection of oxidizing gases.

ACKNOWLEDGMENTS

This work was supported by the Russian Science Foundation (project no. 14–13–01470).

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Translated by Z. Svitanko