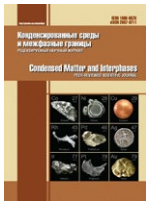

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Phase composition and texture of palladium (II) oxide thin films on SiO_2/Si

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Abstract

The objects of the study are nanostructures based on palladium (II) oxide of various elemental compositions and morphological organization.

The aim of the work is to establish the influence of synthesis conditions on the phase composition and texture of thin films of palladium (II) oxide synthesized by oxidation in an oxygen atmosphere of initial ultrafine layers of metallic palladium of various thicknesses on SiO_2/Si(100) substrates.

Conclusions: It has been established that the oxidation of the initial ultrafine layers of metallic palladium with thicknesses of ~ 95, ~ 190, and ~ 290 nm in an oxygen atmosphere in the temperature range T_{ox} = 873 - 1123 K leads to the formation of homogeneous polycrystalline films of palladium (II) oxide on SiO_2/Si (100) substrates. It is shown that the surface layers of PdO/SiO_2/Si (100) films have a pronounced texture (001), the degree of which increases with increasing oxidation temperature.

Keywords: Palladium (II) oxide, Phase composition, X-ray phase analysis, High-energy electron diffraction, Gas sensors

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1. Introduction

Currently, various types of binary, ternary, and more complex metal oxide semiconductors are being intensively studied as materials suitable for detecting gases with oxidizing properties. In most cases, n-type conduction semiconductors such as SnO_2 [1–3], ZnO [4, 5], In_2O_3 [6], and TiO_2 [7] are traditionally used for this purpose. However, in the last decade, the study of the sensory properties of wide-band metal oxide semiconductors with p-type conductivity and composites based on them has begun [8]. Sensor materials based on Cu_2O [9], NiO [10] nanostructures, porous NiO microspheres [11], and nanostructures based on copper (II) oxide [12] have been synthesized. Nanocomposites with a p-n heterojunction are considered the most promising for the detection of oxidizing gases [13]. Research by scientists of Voronezh State University has proved the effectiveness of using nanocrystalline and thin films of palladium (II) oxide characterized by p-type conductivity [14]. Studies of the physical and chemical properties of n-type metal oxide semiconductors have led to the creation of sufficiently efficient gas sensors based on them [15]. The enormous success in using tin dioxide SnO_2 gas sensors is not least due to accurate information about the nature of point defects (oxygen vacancies), as well as about chemical and physical processes involving adsorbed oxygen molecules and analyzing gases. To date, gas sensors of the resistive type are produced in two ways: thick-film and thin-film technologies. It should be emphasized that thick-film gas sensors are formed by various methods from pre-synthesized nanocrystalline powders. As a result, thick-film polycrystalline structures can be considered isotropic in the first approximation. Therefore, nonstoichiometry, crystallite sizes, and specific surface area are critical physical and chemical parameters that determine the functional properties of sensors. For gas sensors based on thin films, another important criterion is the morphology and orientation of the surface layers, which play an important role in the detection of toxic or explosive gases [15]. Despite the widespread use of palladium (II) oxide in various fields of science and technology, many fundamental properties of this material have not been sufficiently studied, including the formation of thin and nanocrystalline films. Therefore, the purpose of this work is to establish the influence of synthesis conditions on the phase composition and texture of thin films of palladium (II) oxide synthesized by oxidation in an oxygen atmosphere of initial ultrafine layers of metallic palladium of various thicknesses on SiO_2/Si(100) substrates.

2. Experimental methodology

A two-stage process was used to synthesize thin films of palladium (II) oxide. During the first stage, thin films of metallic palladium were formed by open evaporation in a vacuum. The method of open evaporation in vacuum is the simplest way to produce films of various materials. A freshly prepared powder of the sprayed substance is placed in a crucible made of graphite or refractory metal, the substrate is fixed in a heated holder, and the entire system is evacuated. The substrate is heated until its temperature is equal to the required value, and then the temperature of the evaporator is increased. When the time of the spraying process reaches the required value, the flap separating the evaporator and the substrate is closed, after which the substrate with the film cools down in vacuum. In addition, an upgraded film production technology is often used, which uses additional evaporators. In this work, tungsten heaters were used to produce thin films of metallic Pd by thermal evaporation in high vacuum, which were used to heat palladium foil with a basic component content of 99.99 at. %. A high vacuum at a residual pressure level of ~ 10^{-8} mmHg in the working chamber was created using a turbomolecular pump. To establish the modes of the palladium film formation process, its vapor pressure was calculated using the equation:

$$\lg P(\mathrm{Pd^S}, \mathrm{Pa}) = \\ = -\frac{20150}{T} + 13{,}670 - 0{,}419 \lg T - 0{,}302 \cdot 10^{-3} T, \quad (1)$$

where T is the absolute temperature, K.

Palladium metal films were formed on SiO_2/Si (100) substrates. The thickness of the SiO_2 buffer layer was ~ 300 nm. The SiO_2 buffer layer is necessary in order to prevent direct interaction of the palladium metal with the substrate material. The oxidation of palladium metal films in the

temperature range T = 970–1070 K grown on Si(100) substrates without a SiO_2 buffer layer led to the formation of palladium silicide Pd_2Si [14].

Metallic Pd films were grown on a SiO_2/Si(100) substrate without heating in order to obtain ultrafine layers with Pd crystallite sizes from 2 to 6 nm. Such crystallite sizes ensure uniform oxidation to form palladium (II) oxide. The thickness of the initial palladium metal films, determined by scanning electron microscopy during the study of chips of Pd/SiO_2/Si (100) heterostructures, ranged from 95±8 to 300±15 nm. When choosing the modes of oxidation of ultradisperse palladium layers, we were guided by the conditions under which films of lower thickness were oxidized in an oxygen atmosphere. The modes of oxidation of the initial palladium metal films in air are shown in Table 1.

The Pd/SiO_2/Si (100) heterostructures were placed in a tubular furnace at room temperature and then the furnace was heated at a rate of ~ 250 degrees per hour to the desired temperature. After reaching the required temperature, isothermal exposure was carried out for 360 and 480 minutes. As shown in Table 1, in several cases, in particular, at oxidation temperatures of T_{ox} = 773 K and T_{ox} = 973 K, the durations of oxidation in air were 360 and 480 minutes, respectively.

3. Results and discussion

Thin PdO films on SiO_2/Si(100) substrates obtained by thermal oxidation in an oxygen atmosphere of the initial ultrafine layers of metallic palladium with a thickness from 95±5 to 290±15 nm were studied by X-ray phase analysis (XFA). In order to increase the accuracy of calculations of the parameters of the tetragonal lattice of thin PdO films, CoKα radiation was used during X-ray studies. In addition, for the same purpose, thin PdO films were synthesized on SiO_2/Si(100) substrates with a thickness from 95±5 nm to 290±15 nm (Table 1). An increase in the thickness of thin PdO films on SiO_2/Si(100) substrates should lead to a change in the ratio of the reflection intensities of palladium (II) oxide and silicon.

For X-ray studies, PdO/SiO_2/Si(100) heterostructures were selected, thermally oxidized under conditions that allowed the synthesis of homogeneous polycrystalline films of palladium (II) oxide. The experimental

Table 1. Modes of thermal oxidation in an oxygen atmosphere of ultrafine metallic Pd films of various thicknesses and phase composition of samples (according to XRD data) after heat treatment

The thickness of the initial films Pd d_{Pd}, nm	Duration of annealing t, min	Annealing temperature		Phase composition of the samples
		T_{ox}, °C	T_{ox}, K	
95 ± 5	480	400	673	PdO + Pd*
95 ± 5	480	500	773	PdO
95 ± 5	480	600	873	PdO
95 ± 5	480	700	973	PdO
95 ± 5	480	800	1073	PdO
95 ± 5	480	850	1123	PdO
190 ± 10	480	400	673	Pd + PdO**
190 ± 10	480	500	773	PdO + Pd*
190 ± 10	480	600	873	PdO
190 ± 10	480	700	973	PdO
190 ± 10	480	800	1073	PdO
190 ± 10	480	850	1123	PdO
290 ± 15	480	400	673	Pd + PdO**
290 ± 15	480	500	773	PdO + Pd*
290 ± 15	480	600	873	PdO
290 ± 15	480	700	973	PdO
290 ± 15	480	800	1073	PdO
290 ± 15	480	850	1123	PdO

* Intense PdO reflexes and weak Pd reflexes.
** Intense Pd reflexes and a few weak PdO reflexes.

data obtained in the form of bar diagrams of PdO/SiO_2/Si (100) samples obtained by oxygen oxidation of the initial palladium metal layers of various thicknesses are shown in Fig. 1–3. Since the intensity of the Si(400) reflex from the silicon substrate in some cases exceeds the intensity of the strongest reflexes of the palladium (II) oxide film by two or three orders of magnitude, the intensity of the X-ray reflexes is represented in logarithmic coordinates.

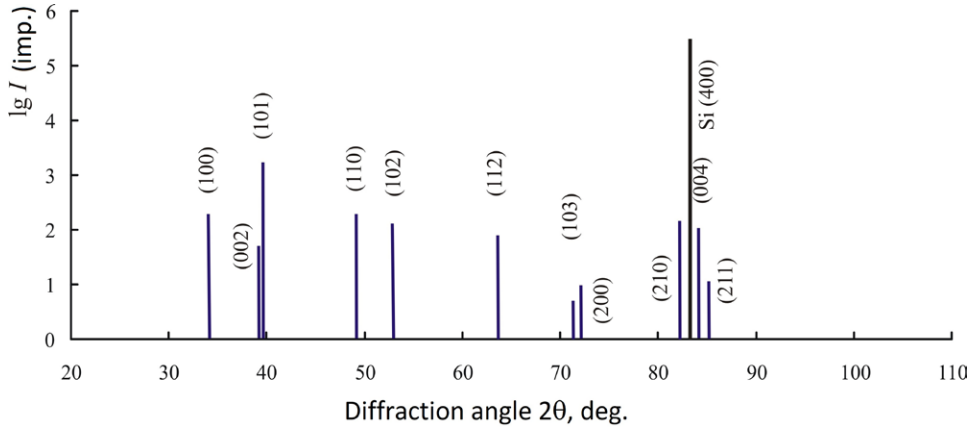

Fig. 1. X-ray diffraction pattern of a nanocrystalline PdO film on a SiO_2/Si (100) substrate obtained by thermal oxidation in oxygen of the initial palladium layer with a thickness of ~ 35 nm at T_{ox} = 1073 K

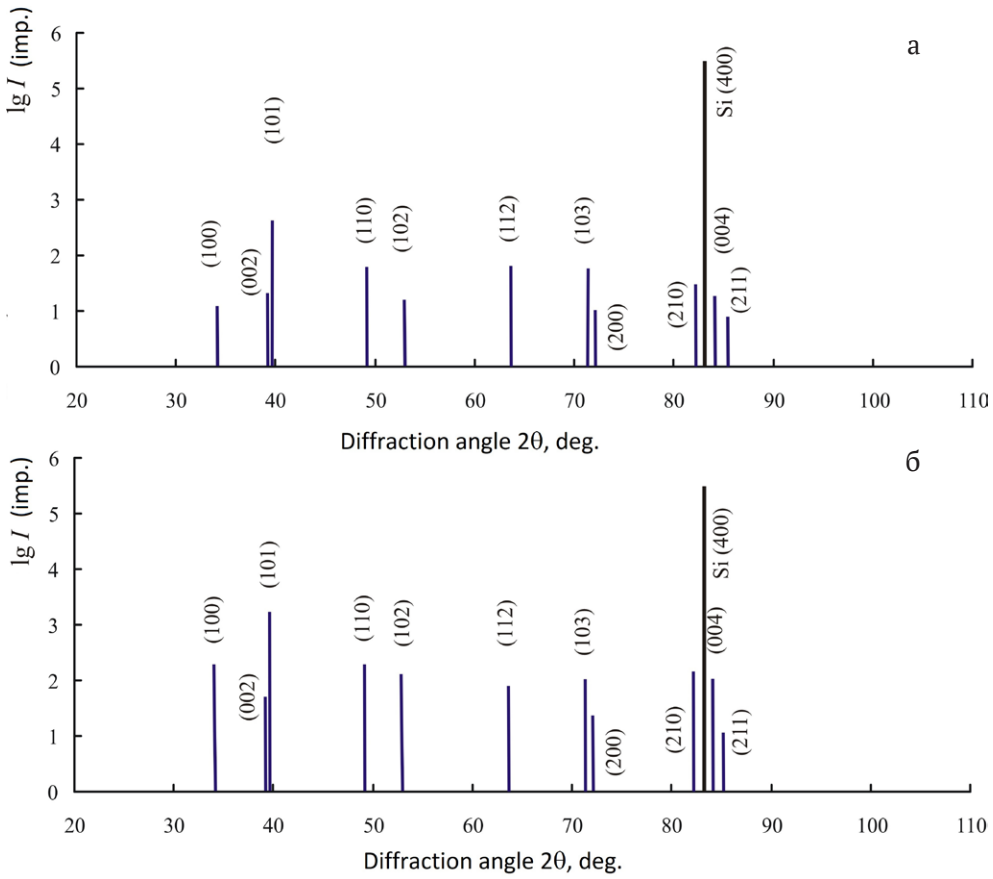

Fig. 2. X-ray diffraction pattern of thin PdO films on a SiO_2/Si(100) substrate obtained by thermal oxidation in oxygen in the initial palladium layer with a thickness of 190 ± 10 nm: a) T_{ox} = 873 K; b) T_{ox} = 973 K

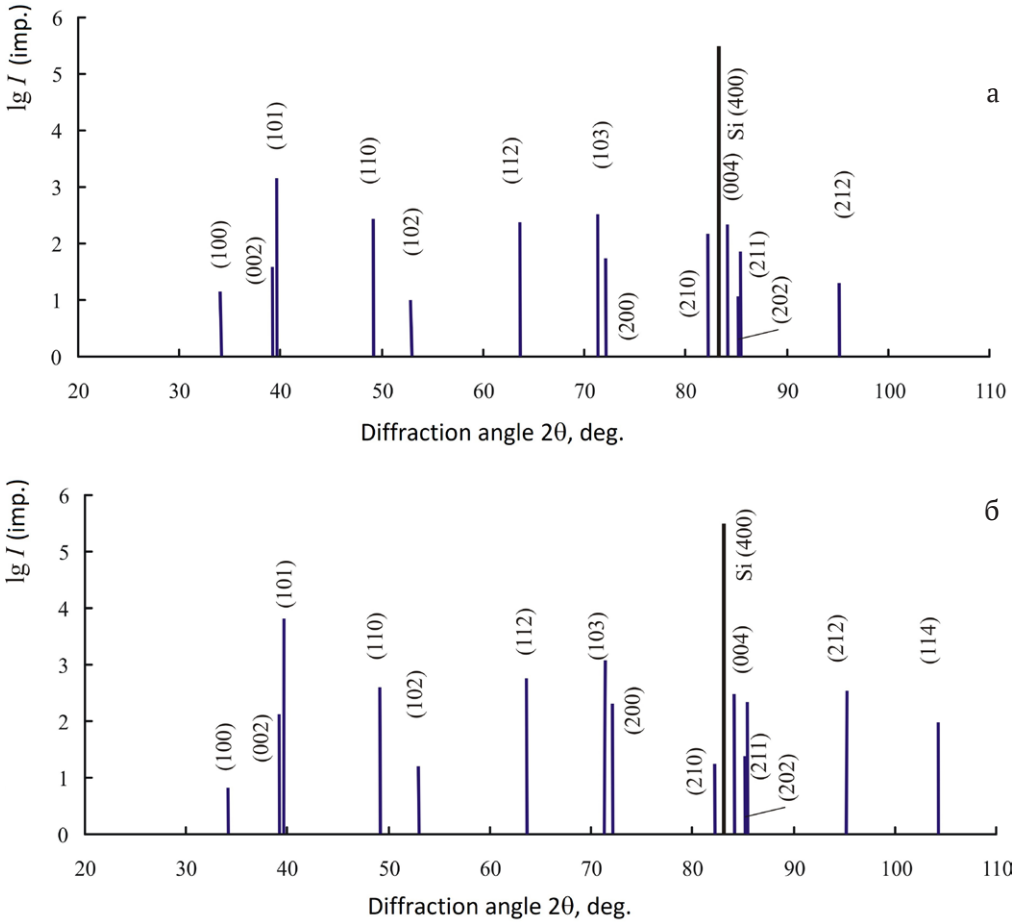

Fig. 3. X-ray diffraction pattern of thin PdO films on a SiO_2/Si (100) substrate obtained by thermal oxidation in oxygen of the initial palladium layer with a thickness of 190±10 nm: a) T_{ox} = 1073 K; b) T_{ox} = 1123 K

When comparing Figures 1 and 2, it becomes obvious that with increasing thickness of the initial ultrafine palladium layers, the intensity of X-ray reflections of palladium (II) oxide films on SiO_2/Si(100) substrates increases. In addition, as can be seen when comparing Fig. 1 and Fig. 3, for palladium (II) oxide films obtained by the thermal oxidation of initial palladium layers with a thickness of ~ 190 nm at T_{ox} = 1073 K, X-ray reflections were recorded at the far diffraction angles, for example, (202) and (212), which did not appear on diffractograms of films synthesized by the thermal oxidation of initial palladium layers with a thickness of ~ 35 nm. Diffractograms of PdO/SiO_2/Si (100) samples synthesized at T_{ox} = 1123 K reveal another long-range reflex (114).

A general analysis of X–ray diffraction patterns of PdO/SiO_2/Si(100) heterostructures obtained by the thermal oxidation of initial palladium layers with a thickness of ~ 190 nm in the temperature range T_{ox} = 873–1123 K allows us to conclude that the synthesized palladium (II) oxide films are single-phase and polycrystalline without signs of any texture. This is evidenced by the ratio of X-ray reflex intensities, which in most cases correspond to similar characteristics of the ASTM standard for a powdered palladium (II) oxide sample [42].

Nevertheless, it should be noted that an increase in the oxidation temperature leads to an increase in the degree of structural perfection of palladium (II) oxide films. This fact is confirmed not only by an increase in the intensity of the corresponding X-ray peaks, but also by the appearance of additional reflections at distant diffraction angles with large values of the Miller indices, for example, peaks (212) and (114).

In order to determine the orientation of the surface layers, PdO/SiO_2/Si(100) samples were

studied by high-energy electron diffraction (HEED), which allows obtaining information from layers several nanometers thick. The electron diffraction patterns obtained during the study of some SiO_2/Si(100) heterostructures are shown in Fig. 4.

A comparison of experimental X-ray diffraction data on the crystal structure over the entire volume of thin films of PdO/SiO_2/Si(100) and the results obtained by the HEED method from near-surface layers allows us to draw the following conclusions. The XRD method captures all reflexes, while the HEED method does not register a number of mixed reflexes (*hkl*) characteristic of a homogeneous polycrystalline palladium (II) oxide film. In addition, with an increase in the oxidation temperature from T_{ox} = 873 K and T_{ox} = 1073 K, along with the disappearance of mixed reflexes (*hkl*), reflexes (002) and (004) become the most intense on electronograms. All this indicates that, unlike the entire volume of thin polycrystalline films of palladium (II) oxide, the surface layers with a thickness of several nanometers acquire a pronounced orientation (001).

The crystallographic planes (001) and (002) in the unit cell of palladium (II) oxide are formed exclusively by palladium atoms, which allows us to conclude that there is a preferential orientation (001) of the surface layers of thin PdO films with increasing oxidation temperature and may be important for the formation of gas sensors with increased selectivity.

4. Conclusion

1. By the X-ray method has been established that the oxidation of the initial ultrafine layers of metallic palladium with thicknesses of ~ 95, ~ 190, and ~ 290 nm in an oxygen atmosphere in the temperature range T_{ox} = 873–1123 K leads to the formation of homogeneous polycrystalline films of palladium (II) oxide on SiO_2/Si (100) substrates.

2. Through the use of the HEED method it has been established that the surface layers of PdO/SiO_2/Si (100) films have a pronounced texture (001), the degree of which increases with increasing oxidation temperature.

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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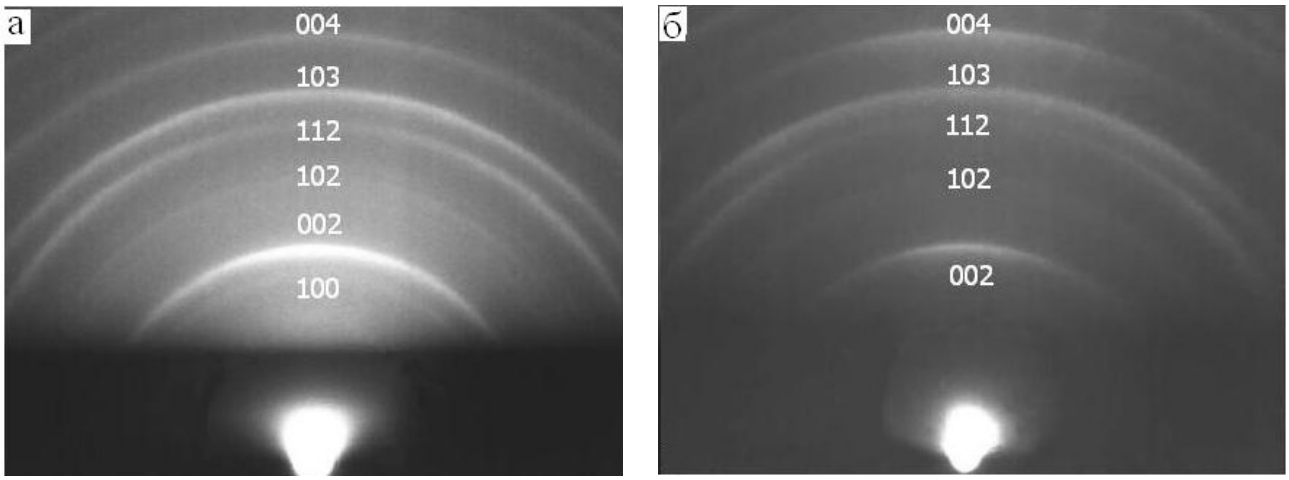

Fig. 4. Electron diffraction patterns obtained with the RHEED method on palladium (II) oxide films synthesized by oxidation in an oxygen atmosphere of the initial ultrafine layers of metallic Pd with a thickness of ~ 190±10 nm: a) T_{ox} = 873 K; b) T_{ox} = 1073 K

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