Conference materials
UDC 620.1.08
DOI: https://doi.org/10.18721/JPM.163.173

Synthesis of thin-film structures of tungsten oxide by the spray-pyrolysis method

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Abstract. Tungsten oxide (WO_3) is a transparent semiconductor material that has been extensively studied for applications in electrochromic windows. Polycrystalline thin films of p-type tungsten oxide (WO_3) were deposited by spray-pyrolysis using tungsten hexachloride (WCl_6) as a precursor. The technological synthesis regimes are considered and the current-voltage characteristics of the obtained coatings are constructed. Films with high porosity, high average surface roughness (67 nm) and low transparency were obtained at a deposition temperature of 280 °C. A WO_3 crystal layer with peaks corresponding to the monoclinic structure was obtained after annealing at a temperature of 400 °C. Higher values of the transmission coefficient are achieved with a decrease in the molarity of the solution and with an increase in the deposition temperature.

Keywords: tungsten oxide, spray-pyrolysis, information-measuring control system, transition metal oxides, electrochromic windows

Funding: This work has been supported by the grants the Russian Science Foundation, RSF 23-29-00343.

Citation: Zinchenko T.O., Pecherskaya E.A., Novichkov M.D., Kozlov G.V., Karpanin O.V., Synthesis of thin-film structures of tungsten oxide by the spray-pyrolysis method, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.1) (2023) 402–407. DOI: https://doi.org/10.18721/JPM.163.173

Материалы конференции
УДК 620.1.08
DOI: https://doi.org/10.18721/JPM.163.173

Синтез тонкопленочных структур оксида вольфрама методом спрей-пиролиза

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Аннотация. Оксид вольфрама (WO_3) – прозрачный полупроводниковый материал, который был широко изучен для применения в электрохромных окнах. Поликристаллические тонкие пленки оксида вольфрама p-типа (WO_3) были осаждены методом спрей-пиролиза с использованием в качестве прекурсора – гексахлорид вольфрама (WCl_6). Рассмотрены технологические режимы синтеза и построены вольт-амперные характеристики полученных покрытий.

Ключевые слова: оксид вольфрама, спрей-пиролиза, тонкопленочная структура, информационно-измерительная и управлящая система, электрохромные окна

Финансирование: Работа выполнена при поддержке грантов Российского научного фонда, РНФ 23-29-00343.

Ссылка при цитировании: Зинченко Т.О., Печерская Е.А., Новичков М.Д., Козлов Г.В., Карпанин О.В. Синтез тонкопленочных структур оксида вольфрама методом спрей-пиролиза // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.1. С. 402–407. DOI: https://doi.org/10.18721/JPM.163.173

Introduction

Tungsten oxide (WO_3) is a transparent semiconductor material that has found wide application in electrochromic windows [1]. Electrochromic transmissive devices require stable conductive materials with high visible light transmittance and good electrotransport properties to switch between colored and bleached states. Regardless of which method is used for deposition, the choice of deposition parameters significantly affects the structure, morphology, and composition of the resulting film, which directly affects the optical and electrical properties of the layer. Films with high porosity or extensive grain boundaries are preferred because they support fast ion insertion-withdrawal, which effectively leads to an increase in staining efficiency and a fast switching speed between the clear and blue states of WO_3 [2]. Reproducibility in terms of stoichiometry, thickness, porosity, composition and crystallinity over a large area is achieved by studying the samples base and identifying the relationship between technological modes and coating properties [3].

The spray-pyrolysis method is widely used for the synthesis of thin-film structures of tungsten oxide. It is based on the use of an aerosol spray of a tungsten oxide solution containing the appropriate precursors to obtain the desired product.

Spray-pyrolysis is one of the most efficient methods for the synthesis of thin films and nanoparticles of various materials. This method makes it possible to obtain high-quality oxide films that have a wide range of applications in various fields, including electronics, catalysis, optics, photovoltaics, and more.

Materials and Methods

Thin layers of tungsten oxide (WO_3) were deposited on electrically conductive antimony-doped tin oxide (ATO), also obtained by spray-pyrolysis [4].

To synthesize thin-film structures of tungsten oxide by spray-pyrolysis, the following steps must be performed:

- Prepare the tungsten oxide solution. To do this, you can use ammonium paratungsthenic acid, which is dissolved in distilled water.
- Prepare solvent for spray. Usually distilled water or isopropanol is used.
- Prepare spray equipment. Usually this is an aerosol generator and a sprayer.
- Apply the tungsten oxide solution on the substrate. Typically, quartz or glass substrates are used.
- Dry the substrate at room temperature.
- Carry out pyrolysis at a temperature of 400 to 800 °C for several hours.
- Cool the substrate and remove a thin layer of tungsten oxide from it.
- Measure the main characteristics of the obtained material, such as thickness, structure, morphology and optical properties.

Figures 1 and 2 show the structure of the information-measuring and control system and the installation layout for the synthesis of thin-film structures.

The deposition of tin dioxide films with different levels of doping with antimony was carried out sequentially in a spray-pyrolysis installation by performing the following operations:

- Placement of the substrate in the reaction chamber of the installation.
- Selection of automatic operation mode in the program designed to control and manage heating.

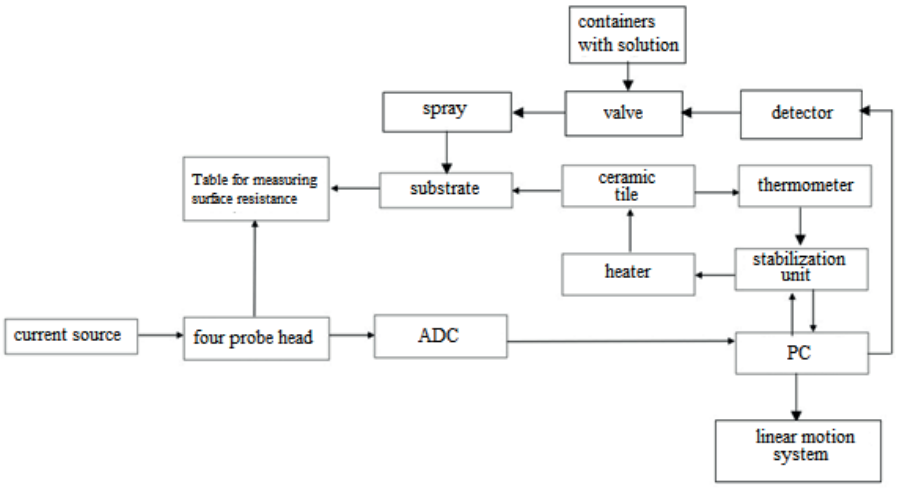

Fig. 1. Structural diagram of the information-measuring control system

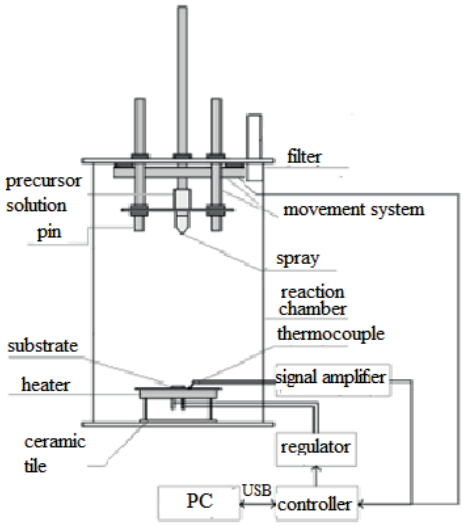

Fig. 2. Model of the experimental installation for spray-pyrolysis [9]

- Input of the heater temperature value (the substrate was gradually heated in the reaction chamber).
- Turn on the compressor to blow air.
- Setting the inlet air pressure in the pneumatic sprayer p = 2 bar using a special regulator on the compressor.
- Opening the ball valve when the set value TS is reached and spraying the prepared solution onto the heated substrate (the valve controls the supply of compressed air from the compressor to the sprayer at the set pressure).
- Close the ball valve and stop spraying the solution (interval between sprays allows the initial set temperature TS to be restored).

Precursor solutions were prepared by dissolving WCl_6 powder in alcohol (C_2H_5OH) containing acetylacetone in a 1:2 molar ratio. Cleaning of 5×5 cm ATO substrates was carried out by degreasing with a pH-neutral detergent, washing with deionized water, and finally ultrasonic cleaning in ethanol for 30 minutes (liquid volume was determined based on the size and number of substrates), followed by drying in compressed air. The quality control of the substrates cleaning by the degree of wettability of its surface (the substrates were lowered into a glass with a new portion of distilled water: on a carefully prepared substrate, the water spreads in an even layer). The following laboratory equipment was used to obtain the solution: fume hood; electronic balance; magnetic stirrer. During the deposition, the substrate temperature and the solution

Table

Conditions for obtaining experimental samples

Sample №	χ, %	C_M, mol/l	V, ml
1	0	0.1	5
2			10
3			15
4			20
5		0.2	5
6			10
7			15

molarity changed successively. Airflow pressure and spray distance (33 cm) were kept constant. The samples were annealed for 4 h at 400 °C to stabilize the crystal coating structure. Table presents the conditions for obtaining experimental samples.

As a result of the experiment, seven samples with different parameters of the solution were obtained, namely, the volume of the solution and the concentration of the precursor. The impurity concentration is 0, since the goal is to obtain coatings with pure tungsten oxide.

Results and Discussion

For samples 1, 2, and 6, two main diffraction peaks corresponding to unseparated (2 0 0) and (2 0 2) grating reflection planes at 2θ ~ 23.6° and 34° characterizing the monoclinic structure were identified. Strong peaks corresponding to the substrate (SnO_2, tetragonal), proving that the WO_3 film is very thin are also identified. A predominant growth was observed along the reflection plane of the grating (2 0 0). Monoclinic WO_3 with predominant growth (2 0 0) was also obtained by spraying a solution containing WCl6 in 50% ethanol and 50% water onto a substrate heated to 300 °C [6]. For sample 3, diffraction analysis shows that the layer is predominantly amorphous, which is a consequence of the high substrate temperature (300 °C) and low gas pressure (100 kPa). Considering the model proposed by Wigie and Spitz [7], the explanation for this is that when low air pressure is used, the droplets do not have enough kinetic energy to reach the heated substrate (at 300 °C) and react because all the solvent is evaporated, and droplets are lost during the deposition process.

The crystallite sizes are the same for samples 1, 2, 4, and 7, which indicate that small temperature differences do not significantly affect the processes of crystal nucleation and growth.

Figure 3 shows the volt-ampere characteristic of sample number 4, since it was obtained at the maximum volume of the solution (20 ml). Such a sample was selected in order to determine the isotropy of a coating of large thickness.

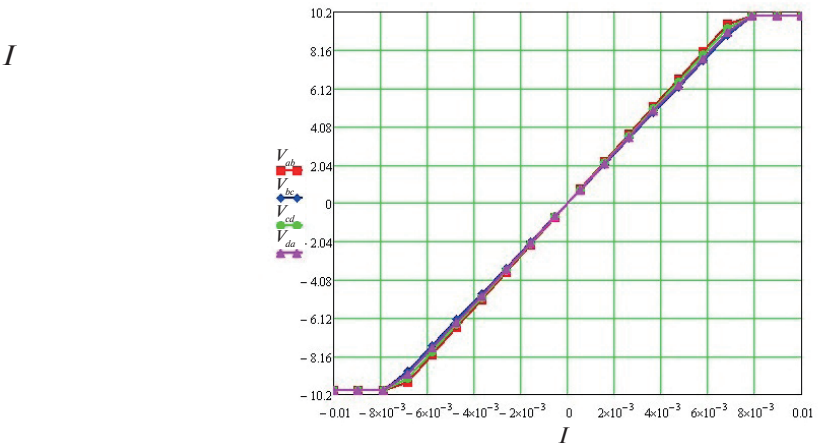

Fig. 3. Current-voltage characteristics of the sample № 4 (WO_3)

Based on the obtained current-voltage characteristics, it can be concluded that the films are isotropic; have the same physical properties in all directions. It becomes clear, since the CVC has a linear dependence, going into saturation and all the branches (for each direction) of the samples are close to each other, and this is allowed by the error.

Due to the formation of a Schottky contact between the gold contacts and the WO_3 layer, it was possible to determine the type of conductivity from current-voltage measurements. For a metal/semiconductor p-type (Schottky) junction to be rectifying, the work function of the semiconductor must be higher than that of the metal [8], a condition that is satisfied by the resulting WO_3 semiconductor layers. The work function of WO_3 is lower than the work function of Au (4.3–4.9 eV and 5.10 eV, respectively). All samples show p-type semiconductor behavior, with sample 6 showing the highest forward conductivity. It is already known that the n-type conductivity of WO_3 is mainly due to oxygen vacancies, which are further responsible for the nonstoichiometry of WO_3 [9]. The balance between the impurity concentration and oxygen deficiency in the lattice affects the n-type conductivity of WO_3 layers. The formation of one or another type of defect depends on the conditions of deposition and annealing (for pyrolysis spraying, these are the deposition temperature and type of carrier gas, annealing duration, temperature and atmosphere). In this case, both deposition and annealing are carried out in air, in a strongly oxidizing environment. At a higher temperature, during annealing in air, most of the oxygen vacancies are reset, forming positive holes, and thus the transition from the n-type conductivity of WO_3 to the p-type becomes possible [10].

Figure 4 shows the dependence of the volume concentration of charge carriers on the impurity concentration in n-type tungsten oxide.

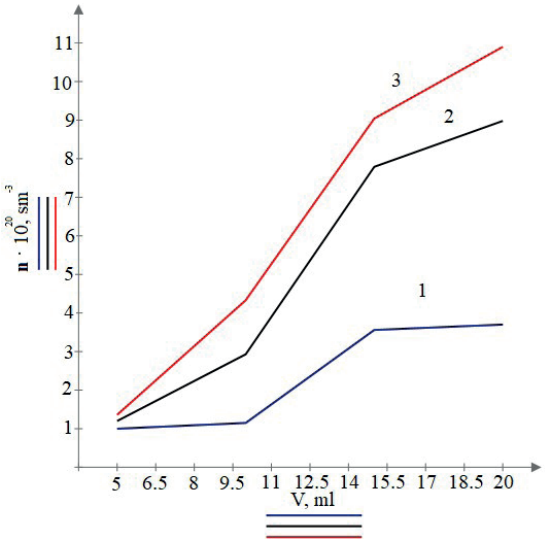

Fig. 4. Dependence of the volume concentration of charge carriers on the volume of the solution

With an increase in the volume of the solution, the thickness of the coating essentially increases. As the thickness of the film increases, the number of free charge carriers increases and the resistance decreases. This is demonstrated by a graph of the dependence of the concentration of charge carriers on the volume (Fig. 4).

Conclusion

Films with high porosity, high average surface roughness (67 nm) and low transparency are obtained at a deposition temperature of 280 °C. The crystalline WO_3 layer with peaks corresponding to the monoclinic structure was obtained after annealing at 400 °C for all samples. Higher transmission values were observed as the solution molarity decreased and the precipitation temperature increased. The WO_3 properties have been found to be highly dependent on surface morphology.

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Received 10.07.2023. Approved after reviewing 11.08.2023. Accepted 18.08.2023.