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Synthesis of thin-film structures of vanadium oxide by spray pyrolysis

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Abstract. Among semiconductors based on transition metal oxides, vanadium pentoxide has generated considerable interest in recent decades due to its wide range of applications. The physical properties of the films depend on certain parameters, such as the level and ratio of dopants, substrate temperature, deposition conditions, heat treatment, substrate material. In this study, it was found that increasing the substrate temperature resulted in an increase in the transparency of the films; as the temperature increased, the microstructure of the film became thinner, leading to an increase in the refractive index; reducing structural defects decreased the extinction coefficient of the films.

Keywords: vanadium pentoxide, spray pyrolysis, information-measuring control system, transition metal oxides

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Синтез тонкопленочных структур оксида ванадия методом спрей-пиролиза

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Аннотация. Физические свойства пленок зависят от определенных параметров, таких как уровень и соотношение легирующих добавок, температура подложки, условия осаждения, термообработка, материал подложки. В данной работе выявлено, что при повышении температуры подложки прозрачность пленок увеличивалась; с повышением температуры микроструктура пленки становится более тонкой, что приводит к повышению показателя преломления; уменьшение структурных дефектов уменьшает коэффициент экстинкции пленок.

Ключевые слова: пятиокись ванадия, спрей-пиролиза, тонкопленочная структура, информационно-измерительная и управлящая система

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Introduction

Among semiconductors based on transition metal oxides, vanadium pentoxide has attracted considerable interest in recent decades due to its wide range of applications [1–3]. Its multivalence, layered structure, wide optical band gap, good chemical and thermal stability, and excellent thermoelectric properties are characteristics that make vanadium pentoxide (V_2O_5) a promising material for microelectronics applications, as well as for electrochemical and optoelectronic devices. It is known to use this material as a catalyst, gas sensors, windows for a solar cell, in electrochromic devices, as well as in electronic and optical switches [4]. Recently, there has been a growing interest in the fabrication of thin-film batteries [5]. Due to its simplicity and low cost, spray pyrolysis is a popular chemical method for producing thin films of a large area. The essence of the method is to spray a liquid onto a surface that is heated to a high temperature. In this case, the liquid evaporates, and the particles contained in it form thin films on the surface [6].

For the synthesis of thin-film structures of vanadium oxide by spray pyrolysis, a solution of vanadium oxystearate is used, which is sprayed onto a surface heated to a certain temperature. In the process of the solution evaporation, oxide particles are formed, which are deposited on the surface in the form of thin films.

In addition, when synthesizing vanadium oxide by spray pyrolysis, various parameters such as temperature, pressure, spraying rate can be changed to obtain structures with different properties. For example, by increasing the temperature, more compact and stable structures can be obtained, and by changing the pressure and spray rate, structures with different sizes and shapes can be obtained.This method is convenient for obtaining uniform and smoother films without pinholes of the required thickness. The physical properties of films depend on certain parameters, such as the level and ratio of dopants, substrate temperature, deposition conditions, heat treatment, and substrate material [7].

Thus, the spray pyrolysis method is an effective method for the synthesis of thin-film structures of vanadium oxide with different properties, which makes it possible to use them in various fields of industry and science.

The aim of this work is the synthesis of thin-film structures of vanadium oxide by spray pyrolysis with the study of their basic properties.

Materials and Methods

Thin films of vanadium pentoxide were deposited on glass substrates by spray pyrolysis using VCl_3 (96%) in 40 cm^3 of distilled water. The spray pyrolysis method makes it possible to obtain vanadium oxide with a high degree of structural organization. The resulting material is characterized by reduced particle size and good crystalline structure.

The solution particles were transferred with compressed and filtered air as a gas carrier onto heated substrates. The nozzle-substrate distance was 32 cm. Before the substrates were placed in the reaction chamber of the installation, their surface was cleaned from possible contaminants that negatively affect the adhesion strength (adhesion). The substrate material was sodium-calcium-silicate glass (window glass) of rectangular shape.

The following substances were used: distilled water; baking soda – sodium bicarbonate ($NaHCO_3$); ethanol (C_2H_5OH); chromium mixture (mixture of concentrated sulfuric acid (H_2SO_4) and potassium dichromate ($K_2Cr_2O_7$)) [8].

The following laboratory equipment was used: fume hood; distiller; ultrasonic bath; electric stove; chemical vessels.

The following operations were performed:

- treating the substrates with baking soda and washing them in tap water;
- ultrasonic treating the substrates in ethanol for 30 minutes (the liquid volume was determined based on the size and number of substrates);
- washing the substrates in distilled water;
- substrates treatment in a chromium mixture heated to 70 °C (the substrates were lowered for 10 minutes into a glass with the mixture);
- washing the substrates in heated distilled water (substrates were lowered into a glass with a new portion of distilled water: water spreads evenly on a carefully prepared substrate);
- drying the substrates on an electric stove when it is heated up to 100 °C.

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.

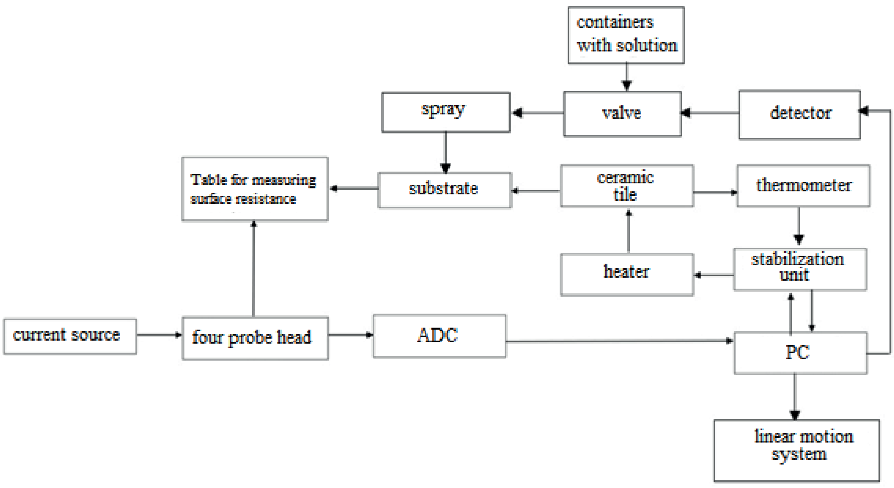

Fig. 1. Structural diagram of the information-measuring control system

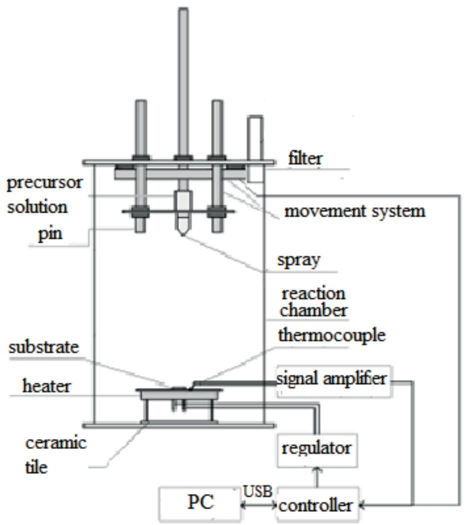

Fig. 2. Model of the experimental installation for spray pyrolysis [9]

Based on the developed structure and created databases, a method for the operation of an information-measuring control system for the synthesis of transparent conducting oxides has been developed:

1. Install the substrate in the holder on the ceramic tile.
2. Using the software, choose the operating mode: manual or automatic.
3. Using the software (on a personal computer), a certain power value P is set.

4. After the signal from the thermocouple has arrived at the personal computer (through the stabilization unit with ADC (analog - to - digital converter), the readings are compared with the values from the thermocouple calibration table.

5. As a result of the comparison, it is necessary to determine the need to increase or decrease power.

6. After stabilization of the temperature regime, choose a container with the required solution and send a signal to the sensor to open the valve.

7. Set the pressure on the compressor and supply air to the atomizer.

8. From the moment you start spraying, the panel starts a stopwatch to control the spraying time.

9. Terminate spraying via control code and turn off the compressor.

Results and Discussion

As the substrate temperature increased, the films transparency increased. As the temperature increases, the film microstructure becomes thinner, which leads to an increase in the refractive index. A decrease in structural defects reduces the extinction coefficient of the films. One of the most common defects is the formation of cracks and defects on the film surface. It is due to the features of the spray pyrolysis process, which is accompanied by hot gases, particle jets, and mechanical stresses, which can lead to the formation of microcracks on the surface and/or inside the film. In this case, it was found empirically that the formation of such defects is primarily affected by the cleaning of the substrates, which was previously described taking into account possible defects and cracking of the coatings.

Another defect that can occur during the synthesis of V_2O_5 films by spray pyrolysis is insufficient adhesion between the material layers, which can lead to the formation of defects in the film structure and a decrease in its mechanical properties. However, the study of the films surface using scanning electron microscopy showed that the films have strong adhesive properties (Fig. 3).

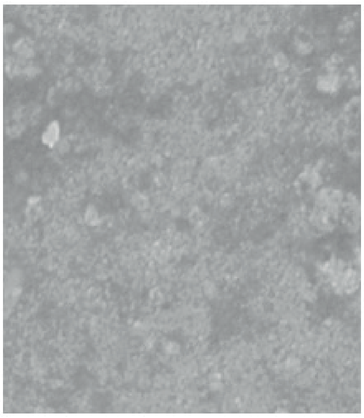

Fig. 3. Image of the coating surface using a scanning electron microscope

It can also be seen that the transmission in the folds is quasi-stable with increasing temperature, indicating that the film morphology gradually improves, thus becoming more transparent. In the range 370–470 °C, a shift of the absorption edge from 2.4 eV to 2.6 eV was observed. As the temperature rises above 300 °C, the phase changes from amorphous to crystalline. Indeed, this increase in temperature leads to higher quality crystalline compounds, resulting in improved mobility and carrier concentration It was found that the experimental data on optical absorption give a linear approximation for indirect allowed ($n = 2$) and direct forbidden ($n = 3/2$) transitions. The optical band gap estimated in the case of an indirect allowed transition was 2.19 eV, and for the direct forbidden transition it was 2.08 eV. For thin V_2O_5 films, the optical band gap can vary from 2.04 to 2.66 eV.

The optical properties of V_2O_5 thin films were studied using transmission spectroscopy. It was found that the films have a transparency of more than 80% and a band gap of about 3.2 eV. The high transparency can be explained by the low concentration of mean band states, which are usually responsible for the absorption of photons with energies below the band gap. Figure 4 shows a graph of the transmittance of samples obtained with different levels of doping.

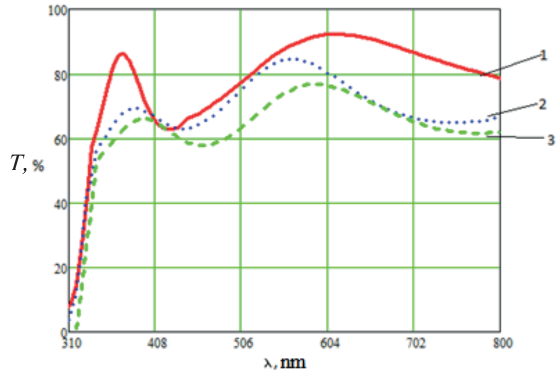

Fig. 4. Transmittance of samples obtained with different levels of doping (volume 10 ml): sample No. 1 (red line) impurity concentration – 0%, sample No. 2 (blue line) impurity concentration – 0.1 %, sample No. 3 (green line) impurity concentration – 0.25%

Several electron scattering mechanisms can operate in TCO (transparent conductive oxide), such as scattering on ionized impurities, neutral centers (point defects and their complexes), thermal lattice vibrations (acoustic and optical phonons), structural defects (vacancies, dislocations, stacking faults), and grain boundaries, depending on the concentration of carriers and the quality of the material crystals . In addition, for doped semiconductors, scattering processes are influenced by such factors as the nonparabolic nature of the conductivity and the formation of impurity clusters.

One of the types of charge carrier scattering in polycrystalline thin TCO films, which can be dominant, is scattering at grain boundaries, which is associated with a rather low electron mobility compared to the mobility in single-crystal samples [10].

Conclusion

Nanocrystalline V_2O_5 films were synthesized using the spray pyrolysis method deposited on glass substrates at various substrate temperatures. The average crystallite size is about 40 nm. It is evident from the experimental results that the crystallite size can be controlled by the deposition temperature. At high temperatures (> 450 °C), chemical bonds, leading to a shift in the absorption edge, were formed at the V_2O_5 film-substrate (glass) interface. Thus, glass substrates are not suitable for deposition at such high temperatures. In this study, the spray pyrolysis method was successfully applied to deposit thin films of V_2O_5 on glass substrates. The resulting films have high optical transparency and band gap, as well as strong adhesive properties. These properties make the material promising for use in various electrochemical devices and catalysts.

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