

## Main technological methods for the synthesis of metal oxides

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**Abstract:** *This article examines the synthesis of metal oxide thin films using sol-gel, deposition, and spray pyrolysis methods. Analysis of sol-gel precursor viscosity shows that 12 hours of aging is optimal for high transparency, while 8 hours is best for achieving low electrical resistance. The study also establishes parameters for spray pyrolysis at 420°C and utilizes Antimony doping to produce high-quality films as alternatives to ITO. These results are recommended for the fabrication of structural elements in field-effect transistors.*

**Keywords:** *metal oxides, sol-gel method, thin films, tin dioxide, zinc oxide, spray pyrolysis, antimony doping, nanostructures, fractal aggregates, viscosity, gelation point, photoelectric properties*

**Introduction.** The synthesis of metal oxides, particularly Tin Dioxide ( $\text{SnO}_2$ ) and Zinc Oxide ( $\text{ZnO}$ ), has become a focal point in material science due to their wide-ranging applications in electronics and optoelectronics. These materials are essential for developing modern devices, such as the structural elements of field-effect transistors. To achieve the desired electrophysical and photoelectric properties, various technological approaches are employed, including the sol-gel method, deposition (dip-coating), and spray pyrolysis.

The sol-gel method is highly regarded for its ability to produce nanostructures at relatively low temperatures compared to traditional chemical homogenization. This process involves the transition from a stable suspension of nanoparticles (sol) to a unified systemic network (gel). The formation and growth of these structures are governed by fractal-structure principles and percolation theory, where the quality of the final product - such as its transparency and electrical resistance - is heavily dependent on the solution's viscosity and aging process.

In addition to the sol-gel technique, deposition and spray pyrolysis offer effective means of producing thin films. However, these methods require precise control over technical parameters, such as withdrawal speeds, rotation frequencies to ensure layer uniformity, and substrate temperatures - typically optimized at 420°C for oxides like  $\text{SnO}_2$  and  $\text{ZnO}$ . Furthermore, the introduction of dopants, such as Antimony ( $\text{Sb}$ ), allows for the creation of low-resistance transparent films that can serve as viable alternatives to more expensive materials like Indium Tin Oxide (ITO).

This study aims to explore the synthesis parameters of  $\text{SnO}_2$  and  $\text{ZnO}$  thin films using these diverse methodologies. By analyzing the relationship between processing conditions - such as precursor concentrations, thermal stress management, and doping levels - this research provides recommendations for optimizing metal oxide layers for high-performance technological applications.

**Literature Review. Sol-Gel Method.** In the sol-gel method, a sol is obtained by introducing specific oscillatory (vibrational) conditions into a homogeneous solution containing all the necessary chemical compounds (alkoxides, organic and inorganic salts). A sol is defined as a stable suspension of nanoparticles that are uniformly distributed throughout the entire volume of the solution without sedimentation.

Over time, nanoparticles begin to aggregate, leading to the formation of voids within the system and the development of a three-dimensional gel network (spatial framework). Upon drying the gel at specific temperatures, the coalescence of nanoparticles results in the formation of nano-objects.

According to modern physicochemical principles, gel formation begins with the development of a sol possessing a fractal structure. Based on flow (kinetic) theory, fractal aggregates grow as a result of particle collisions. Near the gelation point, randomly distributed neighboring clusters - composed of polymers or particle aggregates - interconnect to form a single continuous network.

When a unified cluster network is formed and uniformly distributed throughout the entire volume of the solution, the system reaches the gelation threshold, corresponding to the loss of fluidity. The gelation process can be monitored through changes in the viscosity of the solution. Once the gel is fully formed, the nanoparticles lose their mobility, and this state is referred to as a “wet gel.”

Analysis of the graph shown in Figure 2.5 indicates that the initial stage of gel formation begins approximately 10 hours after the preparation of the mixture solution. At this stage, the gel is no longer completely transparent and gradually becomes opaque (whitish).

At the initial stage of gel formation, the gelation process does not completely cease; instead, a phenomenon known as gel aging occurs. During this process, deformation of the gel network takes place, and the gradual expulsion of liquid from the pores leads to a slow reduction in the overall volume of the gel.

Method. In the sol-gel method, the removal of the solvent from the gel (drying) is of critical importance. Depending on the drying technique employed, different types of materials can be obtained (see Figure 2.5). The dried gel is referred to as a xerogel, characterized by high porosity and a large specific surface area. An aerogel is an ultra-low-density form of xerogel in which the structure of the wet gel is preserved, and the pores are filled with air instead of the removed liquid phase.

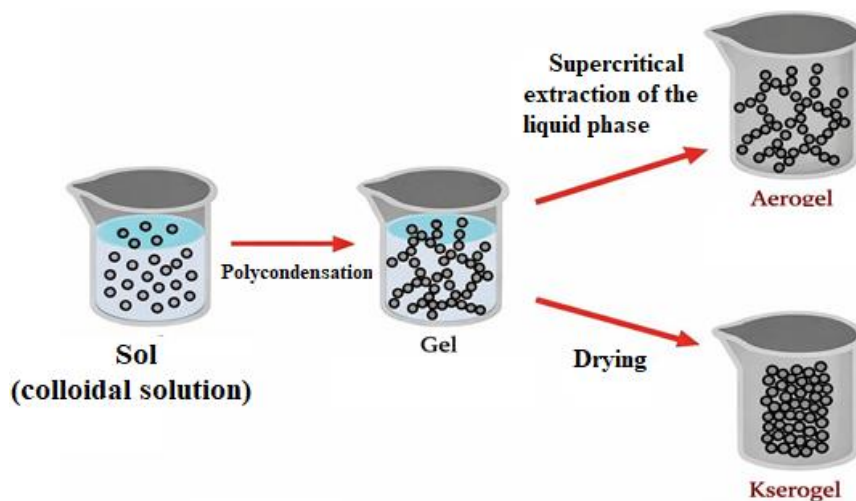


Figure 2.5. Schematic representation of the sol-gel process

Sol-gel technology, due to its ability to carry out processes at relatively low temperatures and to ensure molecular-level homogeneity through the dissolution of salts and oxides in the initial solution, has advantages over many other methods such as chemical homogenization.

Therefore, this technology is considered an efficient method for synthesizing complex metal oxide structures, inorganic-organic hybrid materials sensitive to high temperatures, metastable, luminescent, nanostructured, and surface-modified materials, as well as membranes.

In this research work, transparent thin films of  $\text{SnO}_2$  were fabricated using the sol-gel method, and a set of recommendations was proposed for the development of structural elements of field-effect transistors based on these films.

Additionally, the formation of a gel from a solution of tin chloride in isopropyl alcohol and the time dependence of the viscosity of the solution were investigated. It was determined that the optimal

aging time is 12 hours for obtaining highly transparent films, whereas an aging time of 8 hours is preferable for producing films with low electrical resistance.

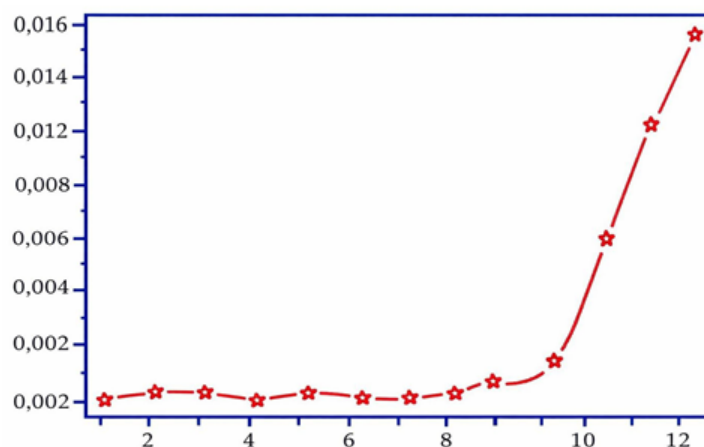


Figure 2.6. Time dependence of the dynamic viscosity of the solution

In addition, thin SnO<sub>2</sub> films were fabricated from the prepared gel using the centrifugal (spin-coating) method, and their electrical and optical properties were investigated. It was determined that films prepared from the chloride-tin precursor solution with an aging time of 12 hours exhibit the best electrophysical and photoelectric properties.

#### Preparation of ZnO and SnO<sub>2</sub> Thin Films by the Deposition Method

The technology for obtaining ZnO and SnO<sub>2</sub> thin films by the deposition method has several distinctive features.

First, during deposition, thickness non-uniformity is always present (radial in spin-coating and linear in dip-coating), which depends on parameters such as viscosity, withdrawal speed, or rotational speed during centrifugation.

Second, in dip-coating, to compensate for thickness variations, the sample must be rotated by 180° after each deposited layer to ensure uniform film formation.

The SnO<sub>2</sub> thin layer was obtained from a 125 ml isopropyl alcohol-based solution. For the synthesis of SnO<sub>2</sub> films, tin(II) chloride dihydrate (SnCl<sub>2</sub>·2H<sub>2</sub>O) with a molar concentration of 0.5 M was used as a precursor. Initially, the solution had a white color; it was then stirred using an IKA RH basic 2 magnetic stirrer at a temperature of 80 °C for 60 minutes until it became completely transparent.

To obtain Sb-doped SnO<sub>2</sub> (SnO<sub>2</sub>:Sb) films, antimony chloride compounds such as SbOCl<sub>2</sub>:HCl or SbCl<sub>3</sub> were used as dopants. The incorporation of SbCl<sub>3</sub> into the SnO<sub>2</sub> solution enables the fabrication of low-resistivity transparent films (SnO<sub>2</sub>:Sn<sub>2</sub>O<sub>3</sub>), which can serve as an alternative to indium tin oxide (ITO) films.

As a result, two transparent tin chloride-based solutions were prepared: doped and undoped precursor solutions with a molar concentration of 0.5 M, containing different antimony chloride contents (1%, 2%, and 4%) in 125 ml volume [19]. These solutions were aged (dried) at room temperature for 168 hours. During this process, the color of the solution changed from transparent to whitish and then to yellow.

Glass substrates were cleaned in an ultrasonic bath using distilled water and isopropyl alcohol.

As substrates, microscope glass slides with dimensions of 2.6 × 7.6 cm<sup>2</sup> (GOST 9284-75 standard) were used. For thin-film deposition, an automatic dip-coating apparatus (shown in Figure 2.7) was employed. The deposition process was carried out at a withdrawal rate of 5 cm/min. As a result, films with an effective surface area of 2.6 × 5.5 cm<sup>2</sup> were obtained.

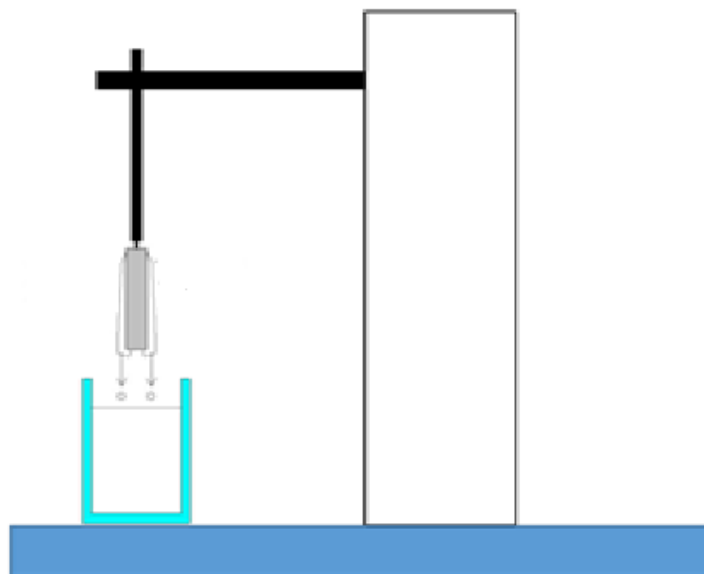


Figure 2.7. Schematic diagram of the dip-coating (deposition) apparatus

Such films were dried in air at a temperature of 360 °C for 2 minutes, followed by slow cooling on ceramic substrates for 2 minutes to prevent the formation of cracks in the substrates due to thermal stress. In this way, 10 layers were deposited for each sample.

#### Preparation of ZnO and SnO<sub>2</sub> Films by the Spray Pyrolysis Method

Using the spray pyrolysis method, thin films were deposited onto microscope glass substrates with dimensions of 26 × 76 × 1 mm (GOST 9284-75 standard). The substrate was heated using an IR ceramic heating element with dimensions of 245 × 60 mm. To minimize temperature gradients across the surface, the glass substrate was positioned at the center of the heater. The temperature was monitored using a Hold Peak HP-1500 pyrometer.

Different temperatures in the range of 300-500 °C were tested, and 420 °C was selected as the optimal temperature for both SnO<sub>2</sub> and ZnO film deposition.

To form oxide layers from the solution, an aerosol was generated using an airbrush (aerograph) with a nozzle diameter of  $d = 0.3$  mm. The airflow for the airbrush was supplied by an oil-free piston compressor (AS-186). The synthesis of SnO<sub>2</sub> and ZnO films was carried out from solutions of the corresponding metal salts.

For the synthesis of tin oxide thin films, tin(II) chloride dihydrate (SnCl<sub>2</sub>·2H<sub>2</sub>O) was used as the precursor, while zinc oxide films were synthesized using zinc acetate dihydrate (Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O). The concentration of metal salts in the solution was 0.25 M.

Distilled water (200 ml) was used as the solvent. To prevent hydrolysis of tin chloride in water, 1 ml of hydrochloric acid (HCl) was added. The solution was then stirred for 30 minutes at room temperature using an IKA RH basic 2 magnetic stirrer.

The simplified schematic of the spray pyrolysis setup for SnO<sub>2</sub> and ZnO thin films is shown in Figure 2.7.

Discussion. Deposition of SnO<sub>2</sub> and ZnO films was carried out at an air pressure of 2 bar and a flow rate of 8 ml/min. The distance between the spray nozzle and the preheated substrate was 35-85 cm (depending on the process conditions).

The SnO<sub>2</sub> thin film was deposited as a single layer over 18 minutes. Multilayer ZnO films were deposited in cycles, with 1-minute deposition intervals followed by 30-second pauses to restore the substrate temperature. Using this method, 14 layers were formed.

The synthesis of Sb-doped SnO<sub>2</sub> (SnO<sub>2</sub>:Sb, 1%) thin films was carried out using a 200 ml isopropyl alcohol-based solution. Tin(II) chloride dihydrate (SnCl<sub>2</sub>·2H<sub>2</sub>O) with a molar concentration of 0.25

M was used as the precursor. Initially, the solution had a milky appearance and was stirred at 80°C for 60 minutes using an IKA RH basic 2 magnetic stirrer until it became completely transparent. Antimony chloride ( $\text{SbCl}_3$ ) was used as a dopant at a concentration of 1 at.%. The deposition of  $\text{SnO}_2\text{:Sb}$  thin films was carried out at an air pressure of 2 bar and a flow rate of 8 ml/min until the solution was completely consumed. The distance between the spray nozzle and the heated substrate was 35 cm.

The film growth process was performed in short pulses of less than 10 seconds, with 20-second pauses between successive spray cycles.

**Conclusion.** Overall, the choice of synthesis method must be aligned with the specific requirements of the application, such as field-effect transistors. The sol-gel method offers superior homogeneity at the molecular level, while spray pyrolysis provides a robust way to grow crystalline oxide layers at controlled temperatures. The ability to tune electrical resistance and transparency through aging time and doping concentrations makes these methods highly versatile for the next generation of optoelectronic devices.

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