

## OBTAINING THIN FILMS OF ZnO THROUGH THERMAL EVAPORATION IN VACUUM AND OXIDATION

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### ABSTRACT

*The paper presents the obtaining of thin films out of ZnO by thermal evaporation and oxidation, in a conventional furnace, at various temperatures between 350-550 °C of films from pure Zn deposited. The influence of current intensity, deposition time and oxidation temperature on film structure and transparency was monitored.*

KEYWORDS: thermal evaporation of zinc, thermal oxidation

### 1. Introduction

Obtaining thin films through physical vapor deposition processes aims to achieve superficial properties of electronic, optical, magnetic, thermal, chemical and mechanical nature.

This involves a sequence of stages such as [1, 2]:

- the production in the working space of a flow of atoms or molecules from the target material to the substrate surface;
- the condensation of the flow of atoms or molecules on the surface of the substrate;
- the germination and growth of the layer.

In the case of thermal evaporation, the transfer of the source material in the vapor phase involves heating it to sufficiently high temperatures that its vapor pressure enables acceptable deposition rates to be achieved. In case of deposition of pure metals, it is necessary that the heating temperature of the source material to ensure a vapor pressure of approx. 1.5 Pa.

Molecules condensed and adsorbed to the surface of the substrate undergo a superficial diffusion process that results in putting them in order and the formation of crystallites, or they may undergo a reversible desorption process.

The zinc oxide has different applications in the manufacture of devices such as solar cells, laser diodes, field-emitting devices, chemical and gas sensors (nanostructured ZnO can increase the properties of gas sensors due to a larger and more reactive surface). Its biocompatibility also makes it attractive for biomedical applications. It has antimicrobial, antiseptic properties and can be used to make dentures. It can provide anti-corrosion

properties, and by adding to organic coatings it improves adhesion and flexibility, also giving shine (gloss).

The thin films nanostructured by ZnO belong to the category of semiconductor materials, with wide energy band, high optical transparency in the visible field, with high chemical and thermal stability, and electrical conductivity in a wide range of values [3, 4].

It has a density of 5.606 g/cm<sup>3</sup>, a melting temperature of 1975 °C, a boiling temperature of 2360 °C, the energy of the forbidden band 3.37 eV, the mobility of electrons at T = 300 K of 200 cm<sup>2</sup>/V s, the mobility of the gaps at T = 300K of 5-50 cm<sup>2</sup>/V s [5-7].

ZnO crystallizes into a hexagonal network of the wurtzite type, Fig. 1 this structure is described as consisting of a sequence of planes composed of ions of O<sup>2-</sup> and Zn<sup>2+</sup>, arranged alternately along the axis of the hexagonal cell C, [5-7].

Within the wurtzite structure considered to be the most stable, the oxygen anions and zinc cations form a tetrahedral unit. The entire structure has no central symmetry.

Regarding the mechanical properties of ZnO, it is a relatively soft material with a hardness of about 4.5 on the Mohs scale. The high thermal and calorific capacity, low thermal expansion and high melting temperature recommend ZnO deposits in many applications [5, 6].

The method of thermal oxidation, used in this work for obtaining ZnO, involves the deposition of layers of pure zinc, by thermal evaporation and their oxidation in air, in a furnace, at different temperatures. The influence of the deposition

parameters and the oxidation temperature on the characteristics of the films obtained was monitored.

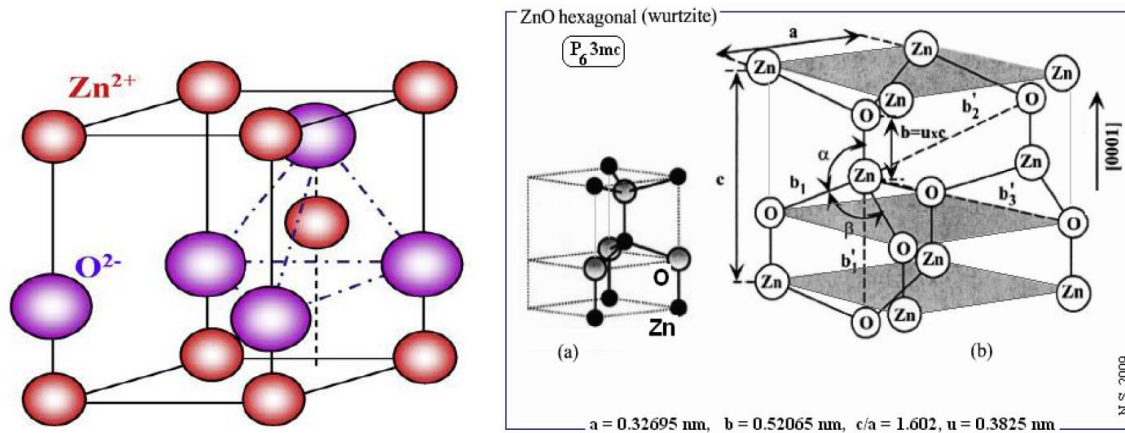


Fig. 1. Crystalline structure of zinc oxide [5-7]

## 2. Experimental conditions

Zinc thin films were deposited on a glass support, by thermal evaporation, the PVD process. For deposits, 99.99% Zn purity target was used.

The pressure in the deposition chamber was in the order of  $4 \cdot 10^{-4}$  Torr. During the deposition process, the glass substrate was kept at the room temperature. The distance between the zinc source and the substrate was of 60 mm. The substrate is rotated continuously to even out the thickness of the deposited film.

In order to obtain quality films, it is important to clean and activate the substrate in order to remove surface impurities, adsorbed gases and to form stable and strong physical and chemical connections between the substrate and the condensed material. In this respect, a chemical cleaning of the substrates was carried out in ultrasonic baths, using 50% ethyl

alcohol. The action was carried out at a temperature of 20 °C, for 60 seconds, followed by rinsing with distilled water and drying.

The oxidation of zinc films was achieved by heating at various temperatures between 350 °C – 550 °C, for 600 seconds.

A number of regimes presented in Table 1 were used to obtain the films.

Microscopic analysis of the films obtained was performed using a Neophot 2 optical microscope with computerized data acquisition.

Before and after oxidation, each sample was subjected to transparency measurements.

Film transparency was determined using an electronic apparatus using a light source and photoreceptor. The light after passing through the deposited film is measured by means of the photoreceptor and an amplifier and the result is displayed with an analogue device.

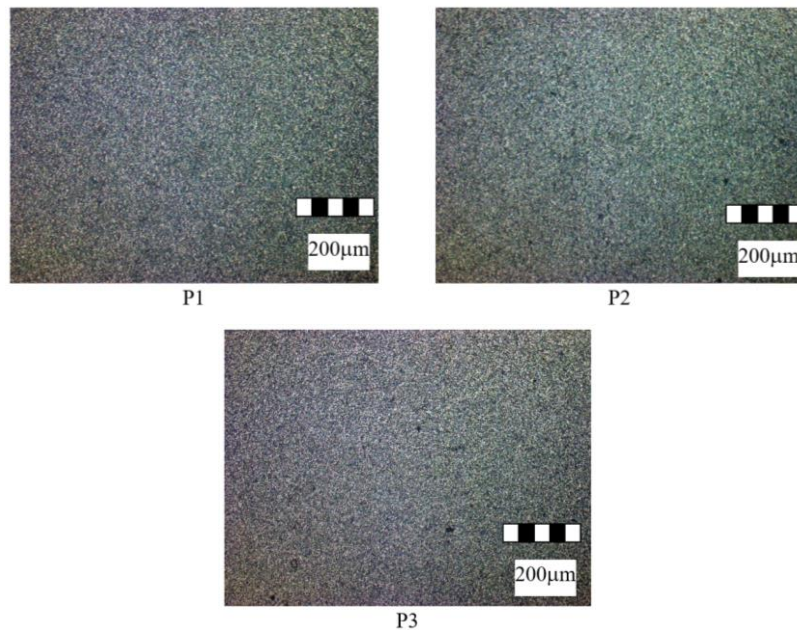
Table 1. Zinc Films-obtaining regimes

Sample Code	Current intensity [A]	Deposition time [s]	Oxidation temperature [°C]	Oxidation time [s]
P1	28	2	420	600
P2	28	3	550	600
P3	28	8	380	600
P4	22	3	350	600
P5	24	3	420	600
P6	28	3	550	600

## 3. Results and Discussion

Analysing Table 1, it can be found that the thermal evaporation deposition process has a short duration due to a high evaporation rate of the target material.

The microscopic analysis performed on the Zn films revealed that they had homogeneous, stable, uniform structures, with a good adhesion to the substrate and without cracks, as can be seen in Figure 2 and Figure 4.



**Fig. 2.** Micrographs of Zn films, deposited by thermal evaporation, for samples obtained at different deposition times P1 - 2 s; P2 - 3 s; P3 - 8 s (constant current intensity)

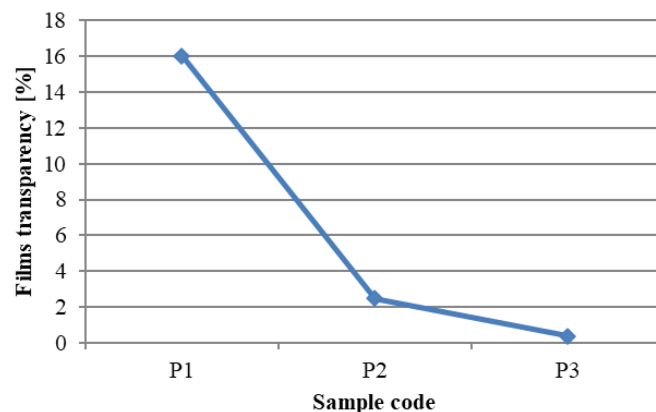
In the case of thermal evaporation, due to the reduced pressure in the enclosure, the mean free path of the particles is greater than the source-substrate distance and they reach the support with the same energy as they have when passing into the vapor phase. The energy of the thermally evaporated particles is low (0.1-0.4 eV), which makes the flux of condensing atoms on the surface of the support bring a low energy input. This will lead to less compact structures.

The purity of the deposited film depends on the quality of the vacuum and the purity of the target.

Collision with waste gases may result in deposits of uneven thickness and impurities.

With the increase of the deposition time, at the same current intensity, there is a slight increase of the granulation, with a tendency of grouping the zinc crystals, Fig. 2.

Following the measurement of the initial transparency of zinc films, P1, P2, P3, a decrease was found with the increase of the deposition time. This is due to the increase in the thickness of the deposited layer, Fig. 3.



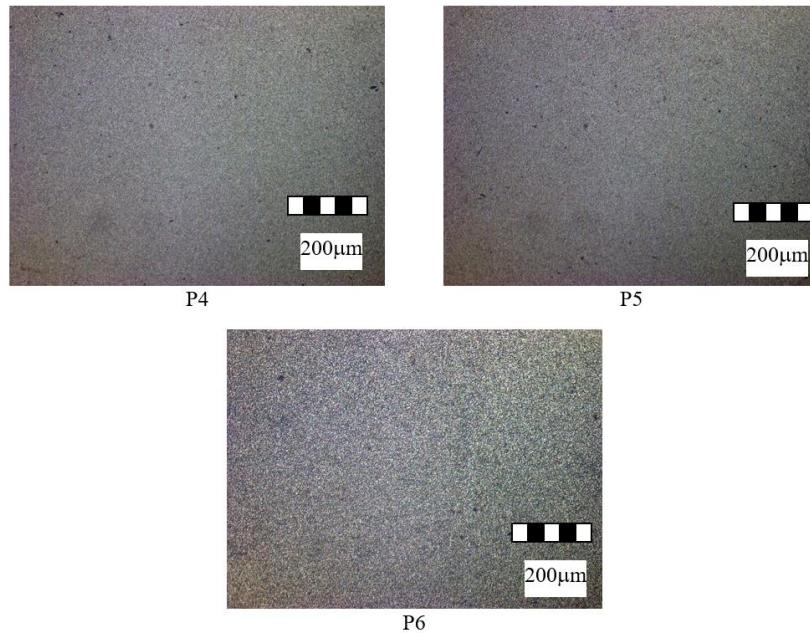
**Fig. 3.** The influence of the deposition time on the initial transparency of zinc films for samples P1 - 2 s, P2 - 3 s, P3 - 8 s

Regarding the influence of the current intensity on the structure of the zinc films deposited, it is found

that at lower current intensities there is a tendency to finish the grain (P4, P5).

At the increase of the current intensity, at the same deposition time, there is a tendency to increase

the granulation, P6 Fig. 4.



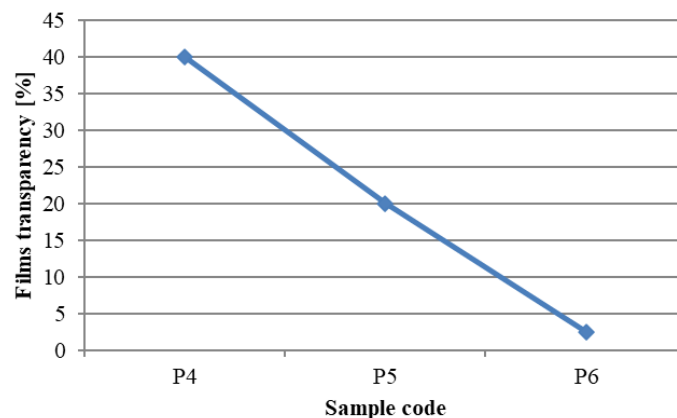
**Fig. 4.** Micrographs of Zn films, submitted through thermal evaporation, for samples obtained at different current intensities P4 - 22 A; P5 - 24 A; P6 - 28 A (same deposition time)

Following the measurement of the initial transparency of the zinc films deposited, a decrease of the transparency at the same time as the increase of the current intensity was found. This is due to the increase in the thickness of the deposited layer, as a result of the intensification of the evaporation - Fig. 5.

The colour of the zinc films deposited is metallic grey and after oxidation in air at different

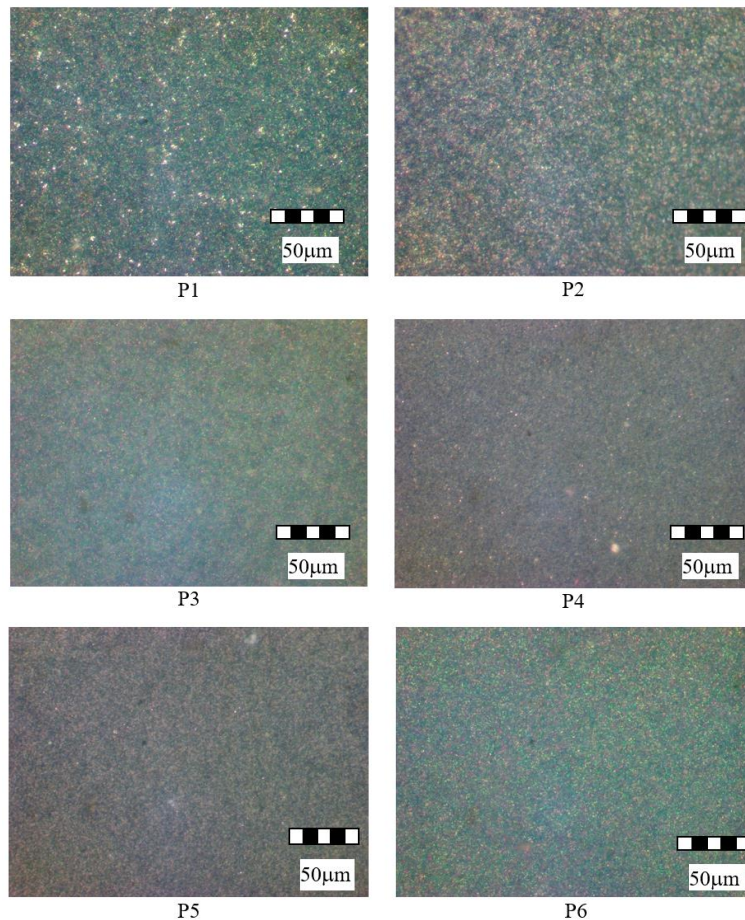
temperatures it becomes lighter as the thickness of the deposition is lower, which indicates the formation of ZnO.

The microscopic analysis performed on Zn films subjected to oxidation at different temperatures, Fig. 6, highlights a slight increase in granulation with the oxidation temperature.



**Fig. 5.** Influence of current intensity on the initial transparency of zinc films for samples P4 - 22 A; P5 - 24 A; P6 - 28 A





**Fig. 6.** Micrographs of ZnO films oxidized at different temperatures

**Table 2.** Transparency of the films

Sample Code	Final transparency [%]
P1	58.8
P2	62.5
P3	55.5
P4	97
P5	80
P6	62.5

With the increase of the oxidation temperature, the transparency of the films increases, which indicates the formation of ZnO (in accordance with the thicknesses obtained), Table 2.

#### 4. Conclusions

Following the experimental researches carried out, the following conclusions can be highlighted:

- obtaining films of ZnO through thermal evaporation and oxidation in air at various

temperatures is a fairly commonly used, economical and non-polluting method;

- low melting point metals may be deposited;
- the pressure in the chamber influences the kinetic energy of the atoms upon their arrival on the substrate, thus influencing the structure of the deposited layer, the density and the porosity;

- a high correlation of deposition parameters is required; their possible variations during the process may lead to non-homogeneities in the chemical composition and crystalline structure of the film; surface irregularities may cause shading effects;

- due to the low energy of the thermally evaporated particles, the deposited films may have a higher porosity and lower density;

- from a structural point of view, the films obtained are uniform, adherent and free from cracks;

- the structure and transparency of the films are influenced by the deposition parameters: the transparency of the films made of Zn decreases with the increase of the deposition time and the intensity of the current due to the increase of the coating thickness;



- transparency of ZnO films increases with increasing oxidation temperature.

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