

EXPERIMENTAL STUDIES OF NANOSTRUCTURED ZnO DEPOSITIONS

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Abstract: Nanoscaled semiconductor has been extensively studied for its potential applications in manufacturing electronic and optoelectronic devices. One of the most important transparent conducting oxides (TCOs) is ZnO in nanoscale configuration. This oxide has been used as highly transparent conducting layers in place of some expensive films in flat panel displays and photovoltaic devices. It has recently been an active field to synthesize ZnO nanostructures via various methods, such as hydrothermal method, high-temperature physical evaporation, high-temperature decomposition, and template method, for various technical and industrial applications. In our work we propose a technique of deposition of ZnO nanostructured powders obtained by two methods via aqueous route for synthesize nanostructured layers. In the second part of the paper, is present a mathematical model for simulating the deposition process and the equipment, designed for experimental study.

INTRODUCTION

Zinc oxide (ZnO) is one of the most important transparent conducting oxides (TCOs) and has attracted much attention due to its unique properties and possible applications in UV light emitting diodes and laser diodes in nanosacle configuration. The band gap of ZnO is very close to that of GaN, and ZnO appears to have similar applications of GaN in optoelectronics. ZnO is already utilized as a transparent conductor [2] in solar cells [3] and is a leading material for transparent transistors [5]. Unless reliable p-type doping can be achieved, however, ZnO will not become economically competitive with semiconductors like GaN. Furthermore, efficient excitonic emission in ZnO should be possible at room temperature due to the large exciton binding energy (60 meV), which is much higher than that of GaN (25 meV) [2]. This indicates that ZnO is a potential material to realize the next generation UV semiconductor laser. In order to develop such optoelectronic devices, the main challenge is to fabricate the low resistivity stable p-type ZnO. It has recently been an active field to synthesize ZnO nanostructures via various methods, such as hydrothermal method, high-temperature physical evaporation, high-temperature decomposition, and template method, for various technical and industrial applications. In our work we propose a technique of deposition of ZnO nanostructured powders obtained by two methods via aqueous route for synthesize nanostructured layers. In the second part of the paper, is present a mathematical model for simulating the deposition process and the equipment, designed for experimental study.[1-3]

EXPERIMENTAL

The hydrolyze of initial powders was performed in a hydrolyze reactor (see figure1). Precursor Zn(II) aqueous solutions were prepared by dissolution of the corresponding nitrides into distilled water. at 90⁰C and pH≈8. The pH of the solution was adjusted to the desired values by mixing with a mineralizer solution with KOH. The hydrothermal synthesis of zinc oxide nanopowders was performed in a 2L computer-controlled Teflon autoclave at 200⁰C and pH≈12 (see figure 2).



Figure 1. Hydrolyze installation

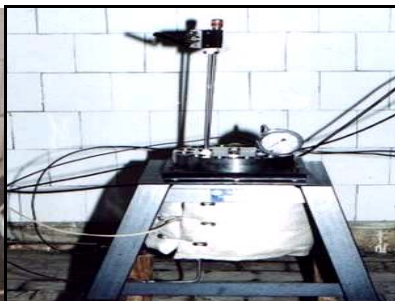


Figure 2. Autoclave

The obtained precipitates were filtered, washed with distilled water to remove the soluble chlorides and ethanol to reduce agglomeration and dried for several hours in air at 100⁰C. The phase composition the powders was investigated by XRD. The mean crystallite sizes were determined using the Scherrer formula. The fundamental equation to determine the size of a crystallite at the intrinsic width of the diffraction ray was formulated by Scherrer:

$$d_m = \frac{k \cdot \lambda}{\delta \cdot \cos \theta}$$
 (1) Where: d_m - mean crystallite sizes; k - constant which depend on the shape of the crystallite, Miller indexes and Bragg demonstrated that its value is near 0.9; θ - Bragg diffraction angle; λ - the wave length of the incident radiation; δ -intrinsic width of the diffraction ray.[3,5]

RESULTS AND DISCUSSIONS

X-ray diffraction phase analysis relieved that the sample synthesizes by hydrothermal route and hydrolyzes at 90⁰C present only the corresponding zinc oxide peaks (according to JCPDS 5-664) like it is shown in figure 3 and 4.

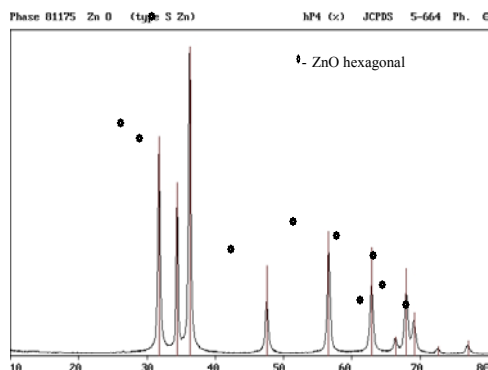


Figure 3. XRD specters of ZnO powders synthesized at 90⁰C by hydrolyze procedure, pH≈8

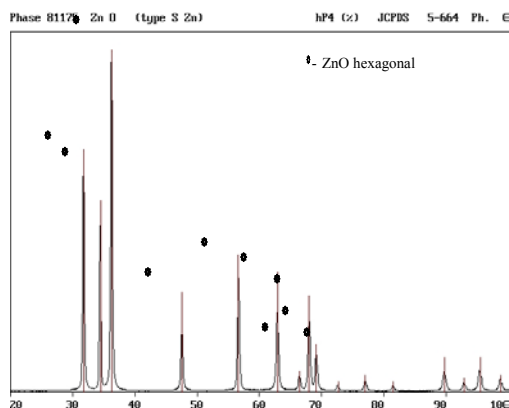


Figure 4. XRD specters of ZnO powders synthesized by hydrothermal route

This means that the powders have crystallized in a hexagonal wurzite ZnO. The crystallite sizes of nanopowders obtained by hydrolyze and hydrothermal route are presented in table 1.

Sample	Conditions	Phase	Mean crystallite size
F1	Hydrolyze, 90 ⁰ C, pH≈8	ZnO, hex.	29.6 nm
F2	Hydrothermal, 200 ⁰ , pH≈12	ZnO, hex.	35.44 nm

Table 1. The crystallite sizes of nanopowders obtained by hydrolyze and hydrothermal route

The analyzing of specters shows that in the case of hydrolyze procedure at an increasing of temperature only the ZnO phase is present. The hydrothermal route offers the possibility in one step.to synthesis ZnO powders in the nanometric range with a better control of process parameters. All the synthesized powders represent the precursors for the deposition process.

MODEL PROPOSED FOR SIMULATE THE DEPOSITION PROCESS

In order to modeling the deposition process of previously obtained ZnO nanostructured powders, we define the function of process:

$$T = f(s, d, p);$$

Where:

T- the thickness of deposition layer, μm ;

s – speed of spray movement, mm/min;

d – distance between spray and support deposition, mm;

p – pressure of jet, bar.

The schema of the deposition process in shown in figure 5.

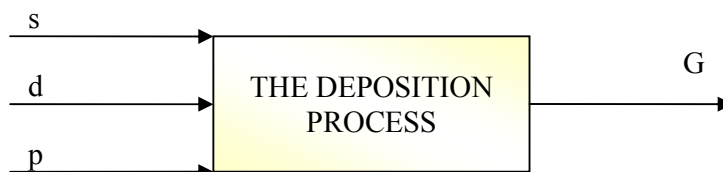


Figure 5. The schema of the deposition process

The mathematical model is:

$$T = k \cdot s^a \cdot d^b \cdot p^c,$$

We have: Variable: s, d, p – known;

Constants: k, a, b, c – unknown;

By a logarithmic transformation we obtain a linear form:

$$\lg T = \lg k + a \lg s + b \lg d + c \lg p$$

We transform:

$$\begin{array}{ll} \lg T = Y & \lg k = A0 \\ \lg s = X1 & a = A1 \\ \lg d = X2 & b = A2 \\ \lg p = X3 & c = A3 \end{array}$$

The model can be treated by a multiple linear regression:

$$Y = A0 + A1 \cdot X1 + A2 \cdot X2 + A3 \cdot X3$$

After a bibliographic analyzes of the deposition methods, we have established the following parameters for the input variables:

$$\begin{array}{ll} s_{\min} = 1 \text{ mm/s} & s_{\max} = 15 \text{ mm/s} \\ d_{\min} = 50 \text{ mm} & d_{\max} = 150 \text{ mm} \\ p_{\min} = 2 \text{ bar} & p_{\max} = 8 \text{ bar} \end{array}$$

For this study a device was designed in CATIA V5.

The device allows us to study the impact of the three parameters: s, d, p. By the movement of the longitudinal luge we can vary the s parameter value. By the movement of the vertical cart we can vary the d parameter value. The spray controls the parameter value of p (see figures 6 and 7).[4]

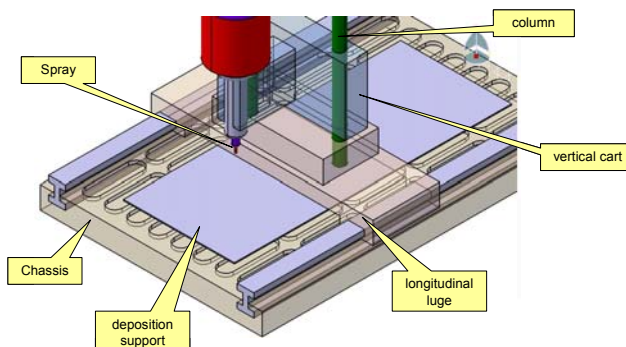


Figure 6. The deposition device

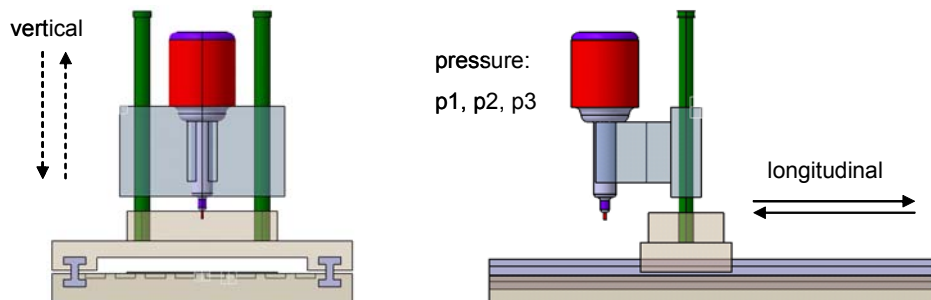


Figure 7. The movements of deposition device

CONCLUSION

Nanomaterials (powders, layers, thin films) possess many unique chemical, physical, and mechanical properties. Due to these beneficial properties, nanomaterials are being favorably considered for a wide variety of structural, non-structural, biomedical, and microelectronic applications and new methods of synthesis are also being discovered almost daily. In our work we synthesized nanopowders and we propose a model to deposit these powders in order to obtain nanostructured films.

Mathematical modeling of the deposition process helps us to identify the functions of process, the variables and the constants that enter into the equation of this function.

The limits of variation for the study parameters and their nature, too, were the basis for designing the experimental process.

This device has a simple construction, being realized in Catia V5. With this device can be deposit a lot of layers of ZnO, at different speeds of movement of the jet at various pressures and at different distances.

This equipment allows a complete study, conducted by an experimental plan.

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