CONTRIBUTION AT 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.*

Keywords: deposition process, semiconductor deposition, deposition simulated.

INTRODUCTION

Nanoscaled semiconductor has been extensively studied for its potential applications in manufacturing electronic and optoelectronic devices. 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.
Zinc oxide (ZnO) has recently gained growing interest due to its unusual electrical and optical properties. ZnO has a wide direct band gap of 3.3 eV at room temperature and high transmittance for visible light. Because of these features, [1]. 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 [4]. 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.
At ambient pressure, ZnO crystallizes in the wurtzite structure (W-ZnO) and transits to the rock-salt structure (RS-ZnO) at about 9.5 GPa. 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.
X-ray powder diffraction (XRD) patterns and field emission scanning electron microscopy (SEM) investigation reveal that large-scale ZnO micro/nanostructured materials have been successfully synthesized via an aqueous method.

EXPERIMENTAL

Precursor Zn(II) aqueous solutions were prepared by dissolution of the corresponding nitrides into distilled water. The hydrolyze was performed in a hydrolyze reactor (see figure1) at different temperatures and pH≈8. The pH of the solution was adjusted to the desired values by mixing with a

mineralizer solution. As a mineralizing agent was used a KOH solution. The hydrothermal synthesis of zinc oxide nanopowders was performed in a 2L computer-controlled Teflon autoclave (CORTEST, USA) at 2000C and pH≈12, using KOH as a mineralizing agent.(see figure 2).

Fig. 1. Hydrolyze installation

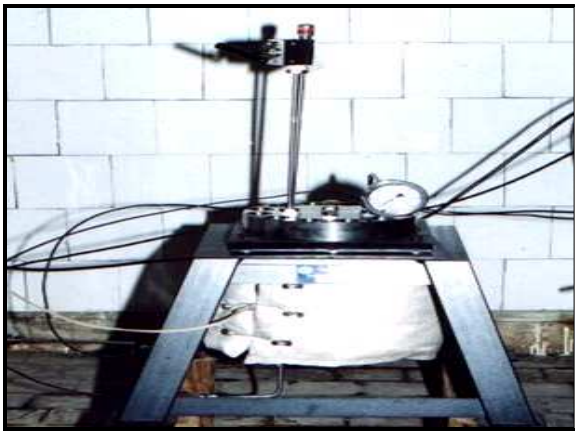

Fig. 2. Autoclave

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 100^0C.
The phase composition the powders was investigated by XRD.
The mean crystallite sizes were determined using the Sherrer formula. The fundamental equation to determine the size of a crystallite at the intrinsic width of the diffraction ray was formulated by Scherrer:

$$d_m = \frac{k\lambda}{\delta \cos\theta} \quad (1)$$

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.

RESULTS AND DISCUSSIONS

X-ray diffraction phase analysis relieved that the sample synthesizes by hydrothermal route and hydrolyze at 90^0C present only the corresponding zinc oxide peaks (according to JCPDS 5-664). The sample synthesize at room temperature, pH≈8, present zinc oxide peaks and $Zn(OH)_2$ peaks (according to JCPDS 1-360).

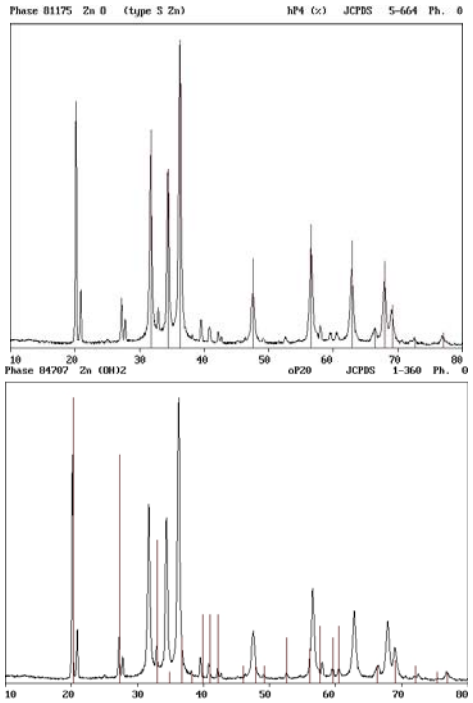

Fig. 3. XRD specters of powders synthesized at room temperature by hydrolyze procedure, pH≈8

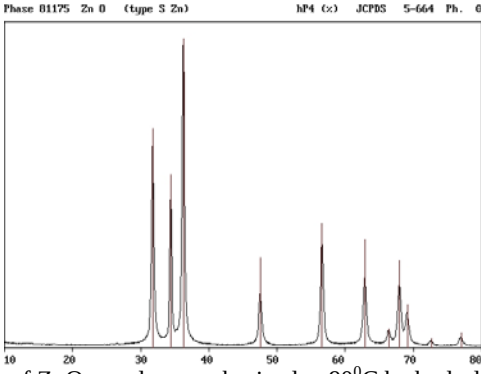

Fig. 4. XRD specters of ZnO powders synthesized at 90^0C by hydrolyze procedure, pH≈8

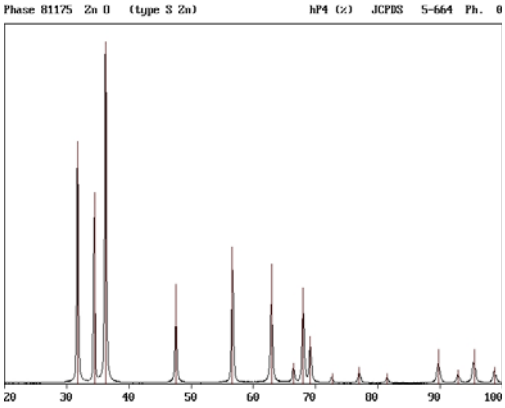

Fig. 5. XRD specters of ZnO powders synthesized by hydrothermal route

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, room temperature, pH pH≈8	ZnO, hex.	21.6 nm
F2	Hydrolyze, 90^0C, pH≈8	ZnO, hex.	29.6nm
F3	Hydtrothermal, 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 spectres shows that in the case of hydrolyze procedure with the increasing of temperature only the ZnO phase is present.
The hydrothermal route offers the possibility to synthesis ZnO powders in the nanometric range with a better control of process parameters.

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:

$$T = f(s, d, p) \tag{2}$$

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 fig…

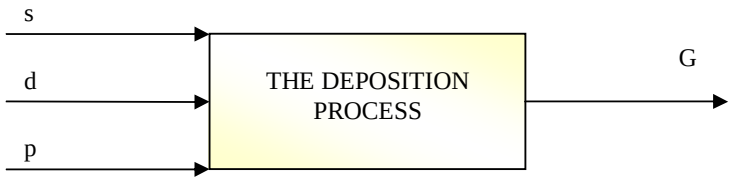

Fig. 6. The schema of the deposition process

The mathematical model is:

$$T = k \cdot s^a \cdot d^b \cdot p^c \tag{3}$$

We have:

Variable: s, d, p – known;
Constants: k, a, b, c – unknown;

By a logarithmic transformation we obtain a linear form:

$$\lg T = \lg k + a \lg s + b \lg d + c \lg p \tag{4}$$

We transform:

lg T = Y	lg k = A0
lg s = X1	A = A1
lg d = X2	b= A2
lg p = X3	C= A3

The model can be treated by a multiple linear regression:

$$Y = A0 + A1*X1 + A2*X2 + A3*X3 \quad (5)$$

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

s_{min}= 1 mm/s	s_{max}= 15 mm/s
d_{min}= 50 mm	d_{max}= 150 mm
p_{min}= 2 bar	p_{max}= 8 bar

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.

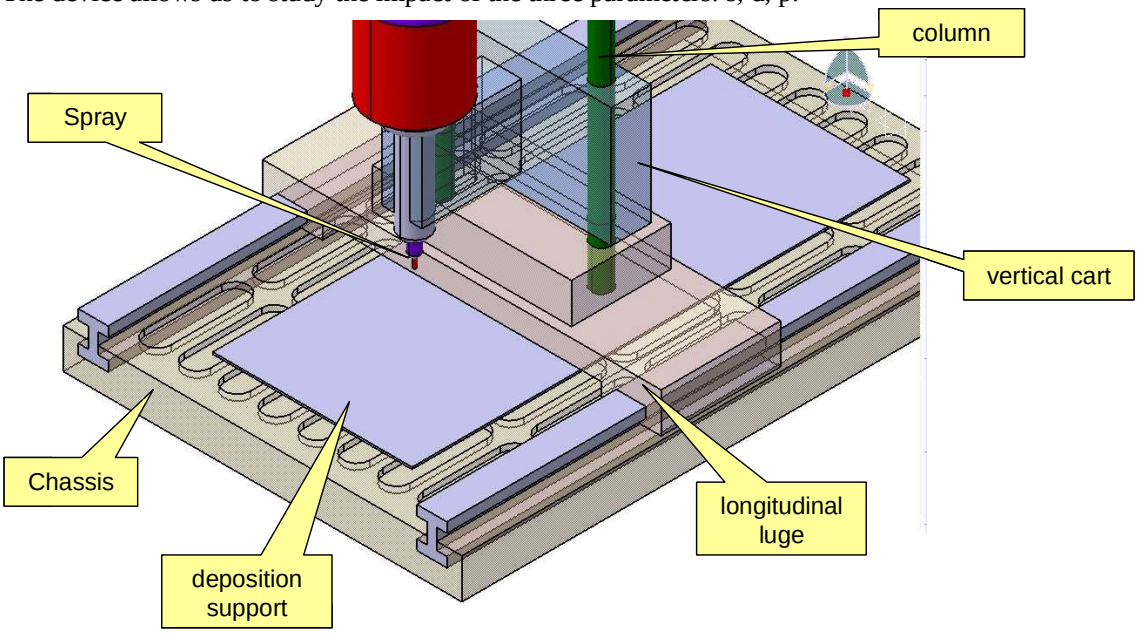

Fig. 7. The deposition device

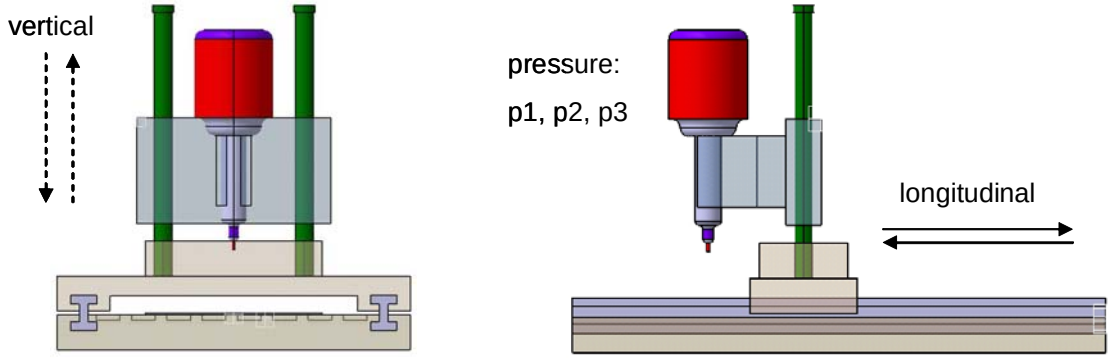

Fig. 8. The movements of deposition device

CONCLUSIONS

Nanomaterials (powders, layers, thins 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 depose these powders in order to obtain nostructured 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 depose 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.

REFERENCES

[1] Norton P., Heo Y.W., et al., *ZnO:growth, doping&procesing* , Materials today, pp.34-40, 2004;
[2] Zhong Wang Lin, *Nanostructures of zinc oxide*, Materials today, pp. 26-32, 2004;
[3] Jiemenez-Gonzalez A.E. et al., *Optical and electrical characteristics of aluminium-doped ZnO thin films prepared bz solgel technique*, Journal of Crystal Growth 192, pp. 430-438, 1998.
[4] Michael B. Kerber, Shafler, Erhard Michael J. Zehetbauer, "*Processing and evaluation of X-ray line profiles measured from nanostructured materials produced by sever plastic deformation*", Rev. Adv. Mater. Sci 10, pp. 427-433, 2005.
[5] Noveanu E., *Metodologia cercetarii experimentale*, Editura Didactica şi Pedagogică, Bucureşti, 2007.