SYNTHESIS OF OXIDE-NANOMATERIALS WITH THE APPICATIONS IN THE MACHINE BUILDING INDUSTRY

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ABSTRACT: Zinc oxide presents a great interest for the scientific community due to its applications in different fields: UV light emitters, varistors, transparent high power electronics, surface acoustic wave devices, piezoelectric transducers, gas sensing and as window material for display and solar cells. New processes for the synthesis and sintering are required to be developed to control and optimize the chemical composition, component distribution, crystalline and grain sizes. In the last decade spray method became a very interesting route for the synthesis of different nanostructured materials as coated and thin films starting from powders prepared by other methods. This paper deals with undoped and doped ZnO nanopowders synthesized by hydrothermal route and sprayed on glass substrate and their characterization.

1. INTRODUCTION

Coating of ZnO nanoparticles on paper surface has potential technological applications. With this motivation, a simple approach of ultrasound assisted coating of paper with ZnO nanoparticles (~20 nm) without the aid of binder is reported for the first time in this work. Due to the combination of interesting piezoelectric, electric, optical and thermal properties ZnO- nanomaterials are of high interest for multifunctional applications in gas sensors, ultrasonic oscillators or transparent electrodes in solar cells. Their implementation and utilisation is strongly dependant on the microstructure and surface nanochemistry characteristics. ZnO is known to be one of the earliest discovered and the most widely applied oxide gas sensing material. Among the functional oxides with perovskite, rutile, CaF2,spinel, and wurtzite structures, ZnO is unique because it exhibits dual semiconducting and piezoelectric properties. ZnO is a material that has diverse structures, whose configurations are much richer than any known nanomaterials including carbon nanotubes. N-type conductivity of ZnO is relatively easy to be realized using Zn in excess or by doping zinc oxide with Al, Ga, In [1]. The most promising dopants for obtaining p-type conductivity are the elements from the V^{th} group. Extensive work on synthesis of ZnO nanoparticles and nanostructures using physical and wet chemical methods has been reported since last decade, with regards to controlling the morphology and properties based on the applications. ZnO nanoparticles deposed like coatings or films on suitable substrates are also important for its potential applications as functional coatings, printing, UV inks, e-print, optical communications (security-papers), sensors, barriers, protection, portable energy, photocatalytic wallpaper with antibacterial activity *etc.* Chemical, thermal, spin coating, spray pyrolysis, pulsed laser deposition methods have been developed to coat on solid supports such as metal, metal oxides, glass or thermally stable substrates. It is well known that purity of ZnO is important for its application necessary needing extreme thermal treatment after its synthesis or coating. Furthermore, employing extreme heat treatment process after coating of ZnO particles on the paper surface is detrimental. For this reason, use of preformed heat-treated ZnO nanoparticles for coating on thermolabile substrates is desirable, although ZnO nanoparticles could be formed/grown on the substrate. New processes for the synthesis and sintering are required to control and optimize the chemical composition, component distribution, crystalline and grain sizes. On the other hand, choice of paper coating technique is an important consideration. However coating techniques mechanical blade or bench coater, rolling, air brush, curtain, spin coating, spray, extruded, print, cast, strip coaters *etc.*, have been used for coating the paper surfaces, some of these techniques, especially contact mechanical techniques cause break, surface defects, variable layer (thickness and composition), consume more material by filling fiber interstices, need excess solvent (water), energy and can affect surface properties, gloss and brightness. Non-impact spray based techniques are generally preferred as these avoid web breaks and streak defects, and have certain advantages in terms of durability and surface quality.

But, these are costly, require maintenance, consume more solvent medium to maintain viscosity and spray quality. Thus, improved techniques compatible with coating on nanoscale and consuming less material are required. Furthermore, with increased emphasis on "green" chemistry, interest has been developed towards adoption and implementation of sustainable processes by minimizing the use of toxic chemicals, solvents, energy *etc.* Thus, development of a non impact coating technique on the verge of "green" chemistry and nanoscience, revitalizing the progress through nanostructuring is crucial.

Recently, spray techiques processing has proven to be a useful technique in synthesis of nanomaterials or metal oxide nanoparticles on suitable substrate.

2. EXPERIMENTAL PROCEDURE

In the hydrothermal synthesis in aqueous solutions, the precursor's aqueous solutions were prepared by dissolutions of the corresponding chlorides or nitrides into distilled water and filtering to eliminate insoluble particles. The process schema is represented in figure 1.The pure ZnO powders were obtained by means of hydrothermal synthesis using $Zn(NO_3)_2$ as precursor and NaOH as hydrolysis agent. The ZnO powders doped with different quantities of Al were obtained using $Zn(NO_3)_2$ and $AlCl_3$ as precursors and NaOH as hydrolysis agent.

The hydrothermal synthesis was performed in a Cortest autoclave at the following parameters: temperature of 200^0C, pressure of 4.5 bars and time of 120 minutes. The precipitated were filtrated, washed with distilled water to remove the soluble chlorides and ethanol to control agglomeration and dried in air at 110^0C. The pH of the solution can be adjusted to the desired value mixing it with a mineralizer solution.

The nanopowder obtained by the hydrothermal method are milled with ethanol and sprayed on glass substrates. The ultrasonic spray nebulizer is placed at a distance of 10 cm above the hotplate. The zinc oxide precursor solution consists of zinc oxide pure and doped in a water/ethanol mixture (ratio 1:3). It is a very simple and relatively cost-effective method for preparing films of any desired composition under controlled conditions, involving the spraying of a solution containing an oxide synthesized by hydrothermal method. In the present investigation the ZnO thin films pure and doped were deposited on properly cleaned glass substrates, all having 2.5 cm × 1 cm dimension and heated at 450^0C.

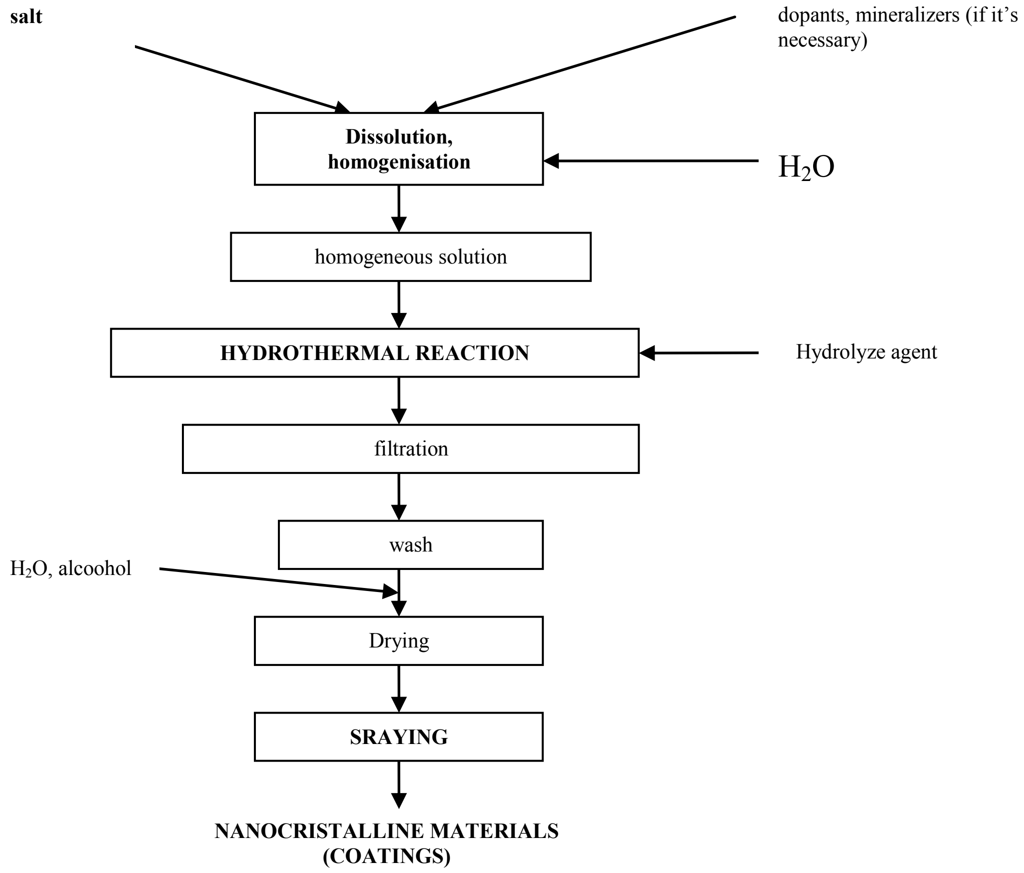

Figure 2. Process schema

X-ray diffraction patterns of the samples were recorded at room temperature with a DRON UM1 θ-2θ diffractometer using CuK*a* radiation and a graphite monochromator, operating at 36 kV and 30 mA in a step scan mode with a step size of 0.05° 2 θ and counting time of 10s per step.

4. RESULTS AND DISCUSSIONS

X ray diffraction phase analysis relieved that the sample synthesizes by hydrothermal route and by spray elaboration present only the corresponding zinc oxide peaks (according to JCPDS 5-664) like in figure2. This means that the powders have crystallized in a hexagonal wurzite ZnO. The crystallite sizes nanopowders and films obtained 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:

$$d_m = \frac{k\lambda}{\delta \cos\theta}$$

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. The grains of elaborated samples are in the range of nanometric scale (d<50nm) and are presented in table 1.

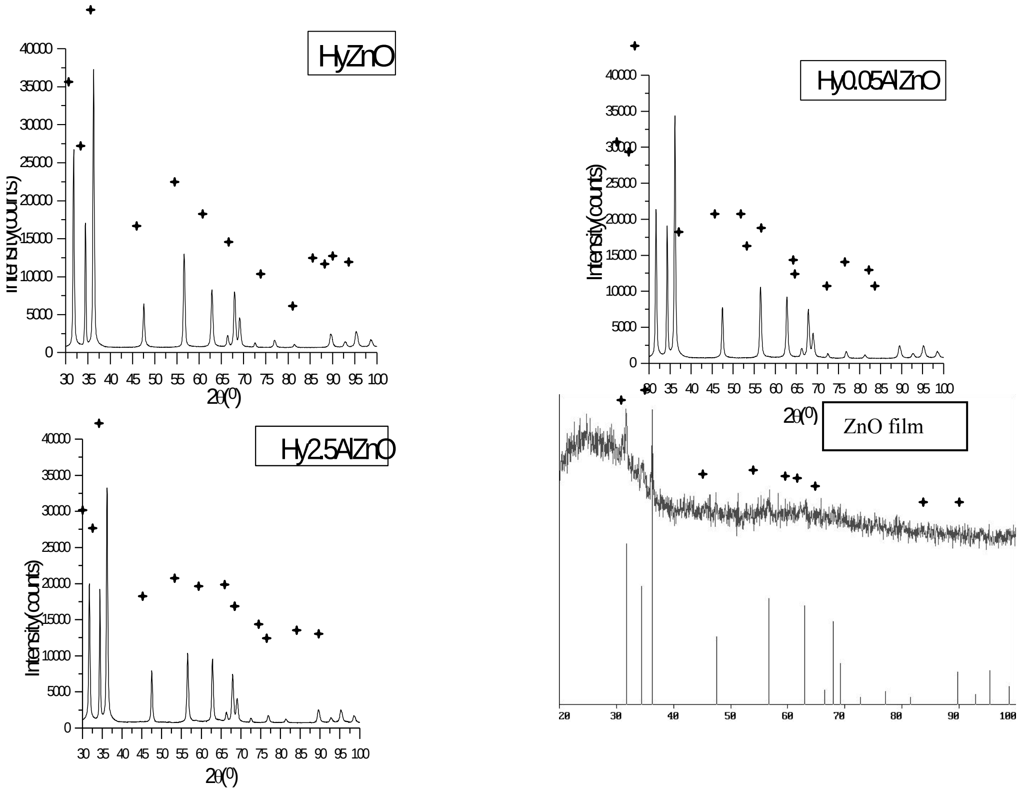

Figure 3. XRD spectres of ZnO powders and film

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

Sample	Conditions	Phase	Mean crystallite size
HyZnO	Hydrothermal, 200^0,pH≈12	ZnO, hex.	23,80 nm
0.05AlZnO	Hydrothermal, 200^0,pH≈12,doped with 0.05%Al	ZnO, hex.	21,90 nm
2.5AlZnO	Hydrothermal, 200^0,pH≈12, doped with 2.5%Al	ZnO, hex.	24,20 nm
ZnO film	Spray elaboration, 450^0C	ZnO, hex	20.10 nm

3. CONCLUSIONS

Concerning all the aspects of the process, the hydrothermal synthesis became in the last decade a very interesting route for the synthesis of different nanostructured materials controlled composition, grain size, and texture witch can be used for another techniques of coatings. Thet spray based techniques are generally preferred to avoid web breaks and streak defects, and have certain advantages in terms of durability and surface quality. This paper demonstrates that can be obtained undoped and doped ZnO nanopowders by hydrothermal route and sprayed on glass substrate under controlled reaction parameters (pressure, pH, temperature, time).

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