RESEARCHES CONCERNING THE ZnO NANOPOWDERS ELABORATION BY SPVD

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Abstract: *The paper presents the results of the experimental researches concerning the technology of elaboration of ZnO nanopowders doped with Al by solar physical vapor deposition (SPVD) starting from precursors obtained by hydrothermal technique. The SPVD was realized using a solar reactor consisting of a glass balloon placed at the focus of a solar PVD furnace. The X-rays diffraction analysis allows a fine nanostructural characterization of all obtained powders. The SEM micrograph and BET analysis complete this nanostructural characterization. Combining the two technologies hydrothermal synthesis and solar PVD method it can be obtained ZnO doped nanophases with controlled composition and morphology (from flower-like structure to nanowhiskers).*

Keywords: nanopowders, elaboration, SPVD, doping, characterization.

INTRODUCTION

Nanopowders are formed of grains (unorganized aggregates, nanocristals or polycrystals) which have nanometric dimensions and belong to the general class of "nanomaterials"[1,2]. The nanomaterials properties are strongly influenced by the interfaces present (surfaces, grain boundaries…).]. Currently, ZnO 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. ZnO is a material that has diverse structures, whose configurations are much richer than any known nanomaterials.
Among the functional oxides with perovskite, rutile, CaF2,spinel, and wurtzite structures, ZnO is unique because it exhibits dual semiconducting and piezoelectric properties. The most significant impediment in developing and exploiting of the zinc oxide based materials in electronic and photonic applications is the difficulty in carrier doping (achieving a p-type material); 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. 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. Different methods routes to obtain ZnO materials were studied: the incorporation of transition metal ions (e.g.V or Cr ions) into a semiconductor photo catalyst by ion implantation or by coprecipitation; introduction of oxygen vacancies by treating a photo catalyst with hydrogen plasma or X-ray irradiation; coupling semiconductors (ZnO or TiO_2) with oxides that enable visible light absorption (WO_3, Fe_2O_3, CdS) by co precipitation or impregnation; doping of N-atoms into the substitution sites in the crystal structure of a photo catalyst. In the science and technology of zinc oxide several key issues have to be achieved [3,4]: controlling the morphology and chemical composition of the zinc oxide powders; purity and particle size during the synthesis process of zinc oxide powders; controlling the level amount of the dopants. Zinc oxide powders with different morphology (prismatic, ellipsoidal, bi-pyramidal, dumbbell-like, nanowire, nanorod) were obtained.
In our paper we present the results on the synthesis of zinc oxide powders doped with different Al content by vaporation-condensation in a solar furnace. The X-rays diffraction analysis allows a fine nanostructural characterization of all obtained powders. The SEM micrograph and BET analysis complete this nanostructural characterization.

EXPERIMENTAL PROCEDURE

2.1. Synthesis of ZnO:Al powders by the vapor condensation method

A reactor powered with a solar energy was applied to evaporate the powder produced the hydrothermal method. The solar physical vapor deposition is an original process to prepare nanopowders. The density of solar flux and the pressure in reactor are presented in the table 1.

Table 1. Conditions of vaporization-condensation process

Sample	Precursors	Solar flux density (W/m^2)	Presure (Torr)
VC[HyZnO]	HyZnO	777	20
VC[Hy0,05AlZn]	Hy0,05AlZnO	910	20
VC[Hy1AlZnO]	Hy1AlZnO	937	20
VC[Hy2,5AlZn]	Hy2,5AlZnO	916	20
VC[Hy10AlZnO]	Hy10AlZnO	853	20

Materials are sublimated inside the evaporation chamber by using solar energy, focused on the sample by means of a 1 m^2 in surface parabolic mirror. Figure 2 shows the solar reactor. The solar furnaces make it possible to implement high temperature material processing. The nanopowders are collected by aspiration on a nanoporous ceramic filter and by condensation on a cold finger.

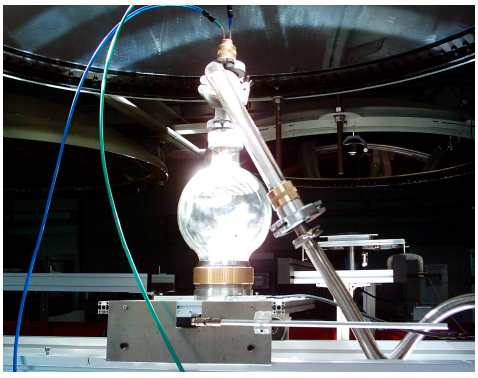
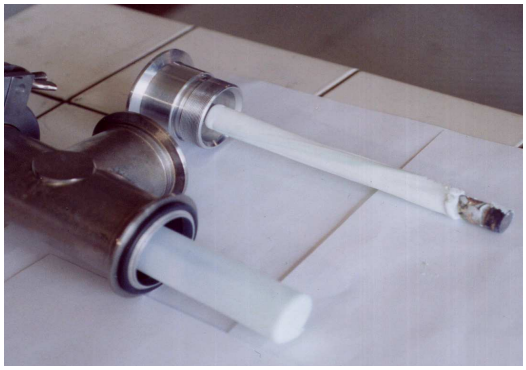
a)  b) 

Fig. 2. a) Vapour condensation reactor
b) Filter and cold finger

Powder phase analysis was investigated by X-ray diffraction analysis using a Phillips Analytical X-ray RV type PW3710700. The fundamental equation to determine the size of a crystallite at the intrinsic width of the diffraction ray was the usual Scherrer equation:

$$L = \frac{K\,\lambda}{\beta \cos \theta} \qquad (1)$$

where L is the mean crystallite size, k the constant which depend on the shape of the crystallite, Miller indexes and Bragg
demonstrated that its value is near 0.9, θ the Bragg diffractionangle, λ the wave length of the incident radiation, the intrinsic width of the diffraction ray.
BET specific surface area of powders was determined on a Gemini 2360 Micromeritics Instruments apparatus. Picnometric density was determined using and AccuPyuc 1330 Micrometrics apparatus. The equivalent mean grain sizes (in nm) were calculated from:

$$d = 6000/(S \times \rho) \quad (2)$$

where S is the specific BET surface area (in m^2/g) and ρ the picnometric density (in g/cm3) of nanopowders. Powder morphology was analyzed by scanning electron microscopy (SEM, Gemini LEO 1530).

2.2. RESULTS AND DISCUTIONS

The intensities of the diffraction peaks correspond to the XRD diagrams of the ICDD reference file (36-1451) and to the zincite structure from the American Mineralogist Crystal Structure Database. The diffraction peaks in the pattern can be indexed to hexagonal wurtzite structured ZnO (space group: P63mc; a =0.3249 nm, c =0.5206 nm). X-ray diffraction phase analysis (Fig.4,5) showed that all the samples, independent of aluminim content, present only the corresponding zinc oxide peaks. The intensity of the peaks relative to the background signal indicates the high purity of the ZnO hexagonal phase of the products. No characteristic peaks of impurities such as Zn(OH)2 were observed in the case of hydrothermal synthesis. Thus, the result showed that the prepared product is single phase hexagonal ZnO. The lattice constants and the grain size for powders made using the hydrothermal method and in the solar reactor were determined from X-Ray Diffraction.

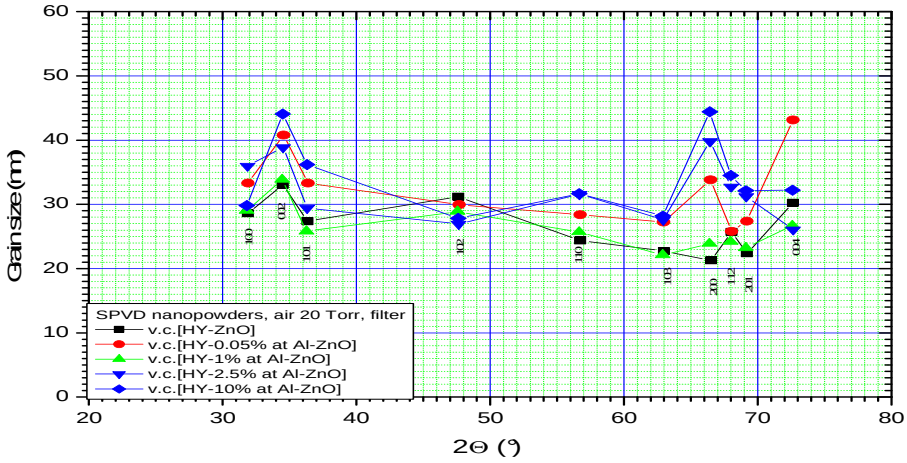
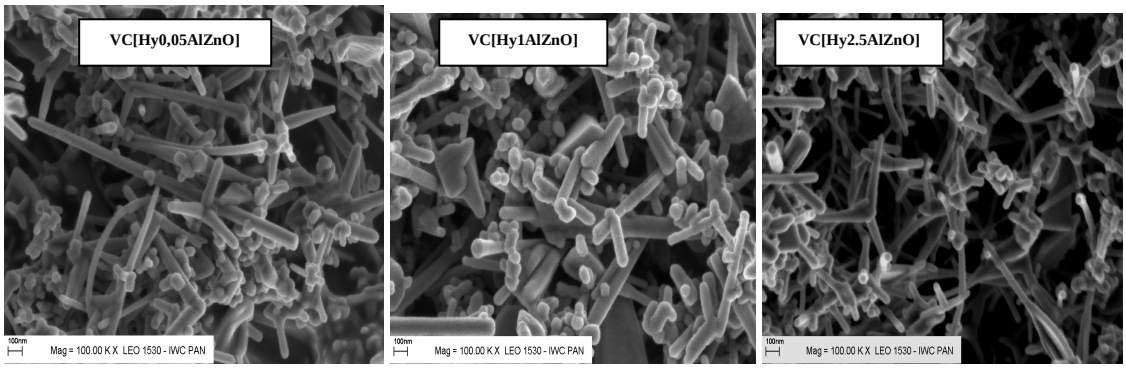


Fig.3. Variation of grain size in function of the crystallographic direction of the powders synthesized by SPVD

The grain sizes from XRD vary with the crystallographic direction. It can be noted the fact that if the 002 peak indicates that the coherency domains are lengthened in the direction of the c axis, a similar phenomenon seems to appear for the 200 peaks of some nanopowders, corresponding to a direction perpendicular to the c axes which is also enlarged. These results, apparently contradictory, could be interpreted as due to a mixture of particles, a part of them being elongated in a direction perpendicular to the c axis, another part parallel to the c axis.
An interpretation of these observations seems to be difficult, three possibilities have been nevertheless examined:
- a departure from stoichiometry change with the solar flux.
- an anisotropic stress effect of surface tension linked to the grain shape.
- a substructure effect linked to the anisotropic growth of nanoparticles.

Anisotropic stresses induced by the surface tension and the grain shape (assumed to be a cylinder in average) could be such that the grain would be in tension along the *c*-axis, that stresses increasing with the shape anisotropy, the radial stresses remaining practically unchanged. The anisotropic shape of grains is experimental evidence. It implies a particle growth mechanism in which defects formed in the basal planes: dislocations loops, twins . . . play an important role. The substructure formed can induce strains changing the average distance between planes in the c direction, this effect being more important when the nanoparticles are whiskers. TEM observations showing that the whiskers are often slightly twisted (see Fig. 4) and their length is larger than the average “grain size” (in fact the substructure size) determined by XRD, are arguments supporting such a hypothesis.



b

Fig.4. SEM micrographs for Al doped ZnO nanopowders obtained by and solar physical vapor deposition

We can observe the formation of zinc oxide whiskers in the physical vapor deposition using solar reactor that demonstrate the influence of synthesis process. The formation of wiskers are specific to the nanomateric range of nanopowdres. The XRD results demonstrate that the nanoparticles have only the hexagonal wurtzite structure. All determinations from BET and grain size determination (XRD) indicate a fine powder after vaporization-condensation process like in figure 5.

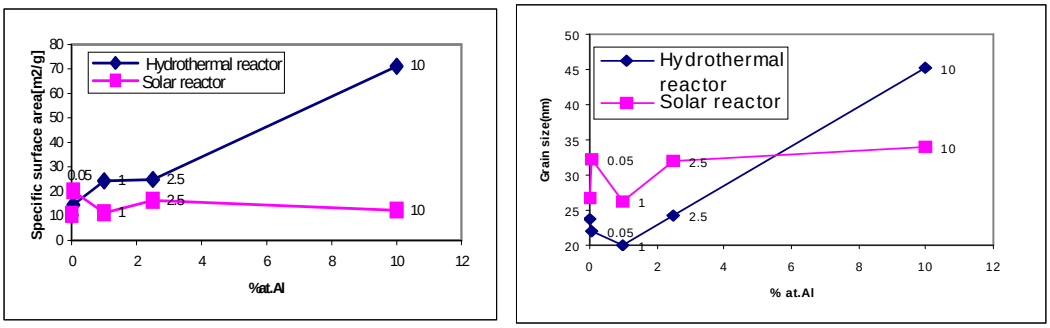


Fig.5. Variation of specific area and of the grain size in function of the synthesis method in function of the synthesis method

For the Al doped zinc oxide powders after solar PVD processing of hydrothermal powders it is demonstrated a lower grain size from the BET of the powders at height percent of aluminum, witch lead the possibility of doping with hight procent of aluminium.

CONCLUSIONS

Nanopowders of Al doped ZnO have been preparedby an original method (SPVD) and their nanostructure characterized by XRD and SEM. Combining hydrothermal synthesis of precursors powders and solar PVD demonstrate that this original method is a powerful method to obtain Al-doped ZnO nanophases with controlled composition and specific morphology (whiskers).

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