Comparative analysis of the morphology of doped zinc and copper oxide nanopowders

E M Modan¹, C M Ducu¹, S G Moga¹, A D Negrea¹ and A G Plăiașu²,*

¹ University of Pitesti, Regional Center of Research & Development for materials, processes and innovative products dedicated to the automotive industry (CRC&D–Auto), University of Pitesti, 11, Doaga, Pitesti, Arges, Romania
² University of Pitesti, Manufacturing and Industrial Management Department, 1, Târgul din Vale, Pitesti, Arges, Romania
Email: gabriela.plaiasu@upit.ro

Abstract. Nano-oxides attracted the attention of the reserchers due to their numerous applications. From this point of view, the development of new synthesis methods has become equally important for industry. The use of solar energy can become one of the ecological methods of obtaining nano-powders. Our paper presents the comparison of the morphology of nanopowders of Al-doped zinc oxide and Mn-doped copper oxide, obtained by physical vapour deposition using solar energy (SPVD), at different pressure and solar flux. The morphological characterization of doped oxide nanopowders synthesized by SPVD was performed by scanning electron microscopy.

1. Introduction
Metal oxides have excellent properties such as: ferroelectricity, high permittivity, superconductivity, magnetism and photoelectricity, and therefore, have been used in various applications, for example in the automotive industry, electronics and electrotechnique, medicine, etc. [1]. Metal oxides, used as gas sensors, are mostly used for detection properties. At present, the most widely applied detection technology is based on electrochemical devices with semiconductor metal oxide that display conductivity changes induced by chemical substances exposure [2]. Nowadays the science and technology of oxide is working on: controlling the morphology and chemical composition of the powders, purity and particle size during the synthesis process of oxide powders and controlling the level amount of the dopants. From metal oxides known with industrial applications ZnO has potential in the numerous fields such as captors and thermocouple couplings, varistors, gas sensors, laser diodes and light emitting diodes especially doped with Al, N and Ga [1,2]. In the same category of metal oxides CuO has applications in various fields such as catalysts, capacitors, photovoltaic cells, field emission, nano-devices and gas sensors. Sensors of this type have proved to be very attractive because they have a high sensitivity to a wide range of gases and a long life. For polycrystalline metal oxide structures used as sensors, electrical resistance is determined by electronic transport through the barriers formed at the contact of two neighbouring crystals [3,5]. Gas sensitivity and selectivity can be controlled by doping or coating the metal oxide with catalytic impurities (Pt, Pd, Au, Ag), changing
the operating temperature or varying the crystallite size of the material [3, 4]. Thus, in the last years, specialists have been more and more interested in the elaboration of specially calculated oxide nanoparticles by physical synthesis. Physical methods have advantages such as: lower working temperatures compared to the solid phase reaction, uniformity of deposition, obtaining a nanostructured thin film by single step (single step method), agglomeration in nanopowders can be avoided, the kinetics of chemical reactions can be controlled by ionizing and dissociating the reactive molecules without increasing the temperature to very high values [6].

2. Experimental studies

2.1. Elaboration of oxide nanopowders

Synthesis by physical deposition in vapour phase using solar energy (SPVD) is an original method for nanopowders elaboration. For the preparation of Al-doped ZnO and Mn doped CuO synthesis, a reactor was used in which a commercial precursor powder target was subjected to solar radiation in argon atmosphere. The precursor powder evaporates and condenses on a nanoporous filter, and then can be collected. The parameters used in the SPVD are shown in table 1.

| Parameters of physical synthesis in the vapour state of oxide nanopowders. |
|---------------------------------------------------------------|
| Precursors (commercial powder) | Synthesis type | Solar flux density (W/m²) | Reactor pressure (torr) |
| ZnO+2,5% mol Al SPVD | 916 | 20 |
| ZnO+10% mol Al SPVD | 852 | 20 |
| CuO+2,5% mol Mn SPVD | 933 | 50 |
| CuO+10% mol Mn SPVD | 933 | 50 |

3. Morphological characterization

3.1. Morphological characterization of ZnO

The morphological characterization of ZnO synthesized through SPVD was performed by Scanning Electron Microscopy (SEM). Electron microscopy is a method of characterization for micron and submicron ceramic powders, whose principle is based on the effects of electron interaction with matter. By SEM it can be obtained the image of a sample by surface scanning with a monokinetic and very fine electron beam. The various interactions that occur at the surface of the sample are transformed by the detector into a signal which is taken over by a cathode ray screen whose scanning is synchronized with that of the electron beam.

The morphology of doped zinc oxide particles changes as a result of vaporization-condensation process from the solar energy reactor. From the analysis of SEM images, one notices formation of whiskers with tetrapod structure, much longer than diameter, in the case of SPVD powders compared with the precursor. The elaborated nanostructured particles are dispersed; they are no longer mixed-up. The morphological study of the powders elaborated through SPVD starting from precursors developed by hydrothermal synthesis was also performed by SEM. For doped ZnO powders with different aluminium concentrations, the particles morphology was analysed before and after the vaporization-condensation process. Micrographs are shown in figures 1 and 2.
Figure 1. a) SEM micrograph of ZnO doped with 2.5% mol Al, commercial.

Figure 1. b) SEM micrograph of ZnO nanostructured vaporized-condensed doped with 2.5% mol Al.

Figure 2. a) SEM micrograph of ZnO doped with 10% mol Al, commercial.

Figure 2. b) SEM micrograph of nanostructured vapour-condensed ZnO doped with 10% mol Al.

From the morphological analysis shown in the figures above it can be observed the change of shape from pellets and spheres (for commercial powders) to whiskers for vapour-condensed, nevertheless of the percentage of doping element (Al). For nanopowders size analysis was used ImageJ software. For the commercial ZnO powder doped with 2.5% mol Al the identified particles in the shape of pellets present sizes between 226-526 nm, thicknesses between 30-45 nm and the spherical particles have a diameter between 29-67 nm like presented in figure 1 a. The obtained data are summarized in the table 2.

Table 2. Experimental results from characterization of zinc oxide nanoparticles.

| Precursors (commercial powder) | Average size (nm) | Shape | Type of synthesis | Average size (nm) | Shape |
|-------------------------------|-------------------|-------|-------------------|-------------------|-------|
| ZnO+2.5% mol Al               | 379               | pellets | SPVD              | 255               | whiskers |
|                               | 44                | spheres |                   | 53                | spheres  |
| ZnO+10% mol Al                | 215               | pellets | SPVD              | 650               | whiskers |
|                               | 64                | spheres |                   | 133               | spheres  |
For nanopowders obtained by SPVD it can be identified whiskers with lengths between 109-426 nm and spherical particles with diameters between 38-77 nm shown in figure 1 b. The figure 2 a presents commercial ZnO powders doped with 10% mol Al, the identified pellets particles present dimensions between 150-358 nm and the spherical particles have a diameter between 52-82 nm. For the nanopowders obtained by SPVD we have identified whiskers with lengths between 311-877 nm and spherical particles with diameters between 91-230 nm like presented in figure 2 b.

3.2. Morphological characterization of CuO

The morphological study for the powders elaborated by solar physical vapour deposition, starting from commercial precursors, was performed by SEM.

For CuO powders doped with different concentrations of Mn, were analysed the particles morphology before and after the vapour-condensation process. For the commercial CuO powder doped with 2.5% mol Mn it can be identified spherical particles with sizes between 49-113 nm revealed in figure 3 a. For the nanopowders obtained by SPVD it was identified hexagonal particles with sizes between 21-51 nm in figure 3 b.

Figure 3. a) SEM micrograph of doped CuO with 2,5% mol Mn, commercial.

Figure 3. b) SEM micrograph of doped nanostructured vapour-condensed CuO with 2,5% mol Mn.

Figure 4. a) SEM micrograph of doped CuO powder with 10% mol Mn commercial.

Figure 4. b) SEM micrograph of doped nanostructured vapour-condensed CuO powder with 10% mol Mn.
For the commercial CuO powder doped with 10% mol Mn, can be detected the spherical particles with sizes between 54-104 nm in figure 4 (a). For the nanopowders obtained by SPVD, figure 4 (b) reveals the spherical particles with a diameter between 10-24 nm and octahedral particles with sizes between 43-81 nm. The obtained data are summarized in the table 3.

Table 3. Experimental results from characterization of cooper oxide nanoparticles.

| Precursors (commercial powder) | Average size (nm) | Shape | Type of synthesis | Average size (nm) | Shape |
|--------------------------------|-------------------|-------|------------------|------------------|-------|
| CuO+2.5 % mol Mn               | 76                | spherical | SPVD          | 35               | hexagonal |
| CuO+10% mol Mn                 | 70                | spherical | SPVD          | 58               | octahedral |

4. Conclusions

Physical synthesis using solar energy demonstrates to be an efficient method for obtaining nanostructured oxides starting from commercially, accessible powders. The morfo-structural characterization using SEM is suitable for obtained nanopowders characterization. The influence of reaction conditions (solar flux and presure) determined important changing of morphology of Al-doped ZnO nanopowders from pellets and spheres to whiskers, as it can be observed in figure 1 and 2. In the case of Mn-doped CuO nanopowders, as presented in figure 3 and 4, the modification start from spherical morphology to hexagonal and octahedral arrangement.

The SPVD process reduces particle size in the same time with morphology modification. The method of elaboration using solar energy proves to be an ecological and innovative method of obtaining nanostructured oxides. The obtained powders can be utilised in future applications for films elaboration, catalyst or electronic devices.

Acknowledgement

We thank the Promes-CNRS, Odeillo, for providing access to its installations, the support of its scientific and technical staff, and the financial support of the SFERA-II project (Grant Agreement no. 228296).

References

[1] Norton D P, Heo Y W, Ivill M P, Ip K, Pearton S J, Chisholm M F and Steiner T 2004 Mater. Today 7 34
[2] Zhong W L 2004 Mater. Today 7 26
[3] Yin M and Liu S 2016 Sens. Act. B Chem 227 328
[4] Zhao X, Wang P, Yan Z and Ren N 2015 Mater. Amst. 42 544
[5] Xu Y T, Guo Y, Li C, Zhou X Y, Tucker M C, Fu X Z, Sun R and Wong C P 2015 Nano Energy 11 38
[6] Plăiașu A G 2018 Sinteza și caracterizarea morfo-structurală a unor oxizi metalici nanostructurați (Pitești: University Press)