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Effects of time exposure and low power sonochemical treatment on ZnO mesostructures

B.C. Costa [a,*], C. Morilla-Santos [b], P.N. Lisboa-Filho [c]

[a] Universidade Estadual Paulista "Júlio de Mesquita Filho" – UNESP, Programa de Pós-Graduação em Ciência e Tecnologia de Materiais, POSMAT, Bauru, SP, Brazil
[b] Universidade Federal do Ceará – UFC, Departamento de Física, Fortaleza, CE, Brazil
[c] Universidade Estadual Paulista "Júlio de Mesquita Filho" – UNESP, Departamento de Física, Bauru, SP, Brazil

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ABSTRACT

A variety of technological applications related to oxide semiconductor-based devices has attracted great interest in the scientific community. Among these materials, zinc oxide (ZnO) has applications in several areas, from light-emitting diodes (LEDs), photovoltaic devices in solar cells and biomaterials. Furthermore, the possibility of application in technological devices highly depends on the synthesis routes employed. Within this context, we investigate the structural and morphological conformation of ZnO structures obtained by low power sonochemical treatment and the effects of time exposure on these mesostructures. To analyze such influences, two samples were prepared without sonochemical treatment with differences in the initial heat-treatment and gas-flux conditions. Another group of six samples was prepared with different time exposures (5, 15, 30, 60, 90 and 120 min) in a low power sonochemical treatment. All the prepared samples were characterized by the XRD associated to Rietveld refinement and SEM. The obtained results analyses indicated that sonochemical treatment was not a necessary condition to obtain highly ordered mesostructures, however, differences in time exposure led to structural and morphological modifications in the ZnO structures. Furthermore, it was observed that the use of vacuum assisted-thermal treatments promotes undesired second phase removal.

1. Introduction

The variety of technological applications related to the development of oxide semiconductor-based devices has attracted great interest in the scientific community, significantly increasing studies related to these materials in the last decades. Among these materials, zinc oxide (ZnO) in particular, has been the object of study of several groups around the world, mainly due to its characteristics of high electronic mobility, high thermal conductivity, wide and direct band gap (3.37 eV at room temperature), large exciton binding energy (60 meV), high chemical stability and recognized antibacterial activity, among others. Such properties make this oxide suitable for a wide range of applications, including its application in transparent thin film transistors, photodetectors, light emitting diodes, laser diodes, gas sensors, varistors, transducers, solar cells, compact cold cathodes, drug carriers, biosensing, treatment and cancer diagnosis, orthopedic coatings and dental implants, among many others [1–8].

It is well known that the properties and, consequently, the applications of a given material fundamentally depend on the applied synthesis routes for its obtainment. Among the chemical routes most commonly employed for the

* Corresponding author.

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obtainment of ZnO, we can mainly highlight the hydrothermal and sol–gel methods [9,10]. Within this context, solution based chemical routes have attracted great interest, since they provide simple and fast improvements under ambient conditions for semiconductor growth with controlled morphology.

The sonochemical method consists of a chemical and ultrasound association. It is a technique that allows for the preparation of a large variety of nanostructured materials, wherein the chemical effects arise from a phenomenon called acoustic cavitation, which can be understood as a process that consists of the formation, growth and implosive collapse of bubbles in a liquid. In this technique, the formed bubbles have a lifetime of microseconds and transient temperatures of 5000 °C and pressures of 1000 atm in located points have been reported, some of these being the characteristics that lead to high energy chemical reactions [11]. This technique is controlled by parameters including amplitude and frequency of applied sound field, temperature, vapor pressure, density of nuclei in solution, and probe emitting radiation geometry [12].

Furthermore, acoustic cavitation acts as a way to concentrate the diffused ultrasound energy to a single set of conditions, providing materials with unique properties from their precursors dissolved in solution [11]. Regarding the ZnO obtained by the sonochemical method, Jung et al. [13] reported the possibility of morphology control since some of the parameters are controlled, such as precursor concentrations and types, and the power and time of ultrasonic irradiation. These authors reported on the achievement of structures with the following morphologies: nanocups, nanodisks, nanorods, nanospheres and nanoflowers.

In addition to providing different morphologies for ZnO, such as ellipsoidal nanoparticles [14], porous nanospheres [15] octahedral nanoparticles [16], besides the previously mentioned structures, sonochemical treatment can also promote morphological and structural modifications in ZnO nanostructures, as already verified in previous studies from our group, wherein ZnO nanoparticles exhibited the emergence of an amorphous shell around themselves after an ultrasonic treatment using a high ultrasonic irradiation power [17,18].

In the present work, we present an analysis related to time exposure of ultrasonic treatment influences on the morphological and structural characteristics of ZnO mesostructures obtained from a sonochemical method using a low irradiation power of ultrasonic waves.

2. Experimental

Aiming to investigate the effects of time exposure of a low power ultrasonic irradiation on the structural and morphological characteristics, six samples were synthesized with the sonochemical method at different times of sonication (t=5, 15, 30, 60, 90 and 120 min). Furthermore, two samples were prepared without ultrasonic irradiation (t=0 samples).

In the present work, t=0 samples were obtained from solutions wherein 4 g of zinc nitrate hexahydrate ($Zn(NO_3)\cdot 6H_2O$ P.A. – Vetec) was dissolved in 300 ml of deionized water. The pH of the solution was then adjusted to 10, with the addition of 9 ml of ammonium hydroxide. This increase in pH value is required since it allows for the formation of Zn^{2+} and OH^- ions in solution, and consequently, the formation of ZnO. The solutions were then left to rest in order to obtain the precipitate. After this period, the pH value observed was approximately 7. The precipitates were then collected and washed five times in isopropyl alcohol and five times in deionized water using a centrifugal Hermle Labortechnik model Z-326, in 15 min cycles at 12,000 rpm. Lastly, the samples were dried in two distinct processes, one was dried in a muffle furnace and air atmosphere at 80 °C for 24 h (ZnO_t-0_80air) and the other was dried in a vacuum oven at 100 °C for 2 h (ZnO_t-0_100vac).

The same solution mentioned above for synthesis of t=0 samples was used for the samples obtained with different time exposures to sonochemical treatment. Six equal solutions were prepared and submitted to sonochemical treatment for 5, 15, 30, 60, 90 and 120 min in a Sonics VCX-750 ultrasonic processor (20 kHz and 750 W) using an amplitude of 40% and an effective power of 25 W. After this treatment, these solutions were left to rest. All samples were washed as previously mentioned and then dried under the same conditions used for the sample without sonochemical treatment and dried in vacuum and named as ZnO_t-5, ZnO_t-15, ZnO_t-30, ZnO_t-60, ZnO_t-90 and ZnO_t-120, respectively, according to the time exposure to the sonochemical treatment time.

In addition, after the analysis of crystallographic data of all samples obtained from the procedure mentioned above, it was realized a blank test, considering this is an important part of sonochemical reactions, since there is a temperature increasing during these reactions. This test was realized in the temperature of optimum time (60 min) of sonochemical reaction (50 °C), taking account that this temperature is related to the exposure time that resulting in better quality sample (higher crystallinity sample). For the blank test, the same initial solution for the synthesis of all samples mentioned above was used. This solution was kept at 50 °C for 60 min. After this time, the heating was turned off and the solution was then left to rest in order to obtain the precipitate, which was washed as all the previous samples and dried in vacuum at 100 °C for 2 h. The obtained sample from the blank test was named ZnO_Blank and the possible morphological changes were checked.

The identification of the crystalline phases of the samples synthesized as described above was performed by X-ray Diffraction using a RIGAKU D/MAX 2100 PC diffractometer. In addition, the Rietveld refinements were done with GSAS [19] and the interface of EXPGUI [20]. Furthermore, morphological analyses were carried out by Scanning Electron Microscopy using a JEOL microscope model 7500F with theoretical resolution of 1 nm Table 1.

3. Results and discussion

Fig. 1 shows the powder diffraction patterns for the samples. According to this figure, it is possible to note that, except for the ZnO_t-0_80air and ZnO_t-0_100vac