

Extraction of Zinc oxide Nanopowders Prepared by Physical Vapor Deposition Technique

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Abstract

In this work, the effects of different extraction parameters on the particle size of the nanopowders extracted from zinc oxide thin film samples were studied. These nanopowders were obtained by the conjunctional freezing-assisted ultrasonic extraction method. Results showed that extraction parameters such as freezing temperature, ultrasonic frequency and application time are very effective in determining the nanoparticle size, which is very important for many applications and uses of highly-pure nanomaterials and nanostructures.

Keywords: Zinc oxide; Nanopowders; Structural phase; Reactive sputtering; Extraction technique

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1. Introduction

Typical breakthroughs in spectroscopic and photonic applications are continuously satisfied when highly pure nanomaterials are employed. For example, zinc oxide nanoparticles can be perfect nanophotonics when no other material exists in the fabricated device as this quantum activity is individually attributed to the zinc oxide [1,2]. Similarly, quantum dot photonic devices (QDPDs) are critically sensitive to the presence of any material with the active nanomaterial [2,3]. Hence, the small contribution may result in a big effect on the device operation. Accordingly, measurements and characterization tests should be carried out with as much as possible guarantee that the prepared nanomaterial is highly pure [4].

Minimizing the probability of existing substrate's material in the extracted material makes any method or technique with such advantage most preferred in nanomaterials and nanotechnology. Unfortunately, mechanical methods cannot overcome this problem for accurate structural and spectroscopic applications [5]. Thermal methods are obviously avoided because the consequent increase in nanoparticle size is not desired at all [6]. Chemical methods are also avoided because they definitely include

some reactions with tiny particles forming very large area (nanosurfaces) [7].

A recently invented method – known as conjunctional freezing-assisted ultrasonic extraction method – submits a highly efficient tool to get nanopowders from thin film samples without any probability to detect residual from substrate's material in the final product. However, the operation parameters of this method can reasonably affect the nanoparticle size. Therefore, further more typical jumps can be made in nanomaterials and nanotechnology as the nanoparticle size is sufficiently controlled [8].

In this work, the effects of some operation parameters of conjunctional freezing-assisted ultrasonic extraction method, such as freezing temperature, ultrasonic frequency and application time, on the particle size of extracted nanopowders are studied.

2. Experimental Part

A dc reactive sputtering system was used to deposit nanostructured thin films on nonmetallic substrates. The operation parameters and preparation conditions of these samples were separately optimized. More details on the specifications and

operation of this system can be found elsewhere [14-16].

Highly-pure (99.99%) zinc sheet was used as a sputter target to be maintained on the cathode of the discharge system. Argon gas is used to generate discharge plasma while the oxygen is used as reactive gas to form zinc oxide molecules. The mixing ratio of argon and oxygen could be precisely controlled in a gas mixer before pumped into the deposition chamber. The discharge electrodes could be cooled using a cooling system employing water as a coolant. The crystalline phase of zinc oxide nanostructures could be determined by controlling the operation parameters of magnetron sputtering system, especially gas mixing ratio, oxygen content in the gas mixture, and anode temperature. The anode was cooled in order to avoid the thermally-induced changes in the structure of the prepared material. Without cooling, the anode temperature might reach 150-180 °C. Using electrical heater on the anode can raise its temperature to 400 °C, which sufficiently induces the structural changes.

As the deposition time is varied, the thickness of the prepared film is proportionally varied. Film thickness was measured by laser-fringes method. The nanopowder was extracted from thin film samples by the conjunctional freezing-assisted ultrasonic extraction method. Full description and specifications of this method can be introduced in reference [8]. The structural properties of the extracted nanopowders were determined by x-ray diffraction (XRD), Fourier-transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and atomic force microscopy (AFM).

3. Results and Discussion

Figure (1) shows the variation of nanoparticle size of the three different samples prepared in this work with the deposition time, which determines film thickness. As the deposition time is increased, the film thickness is increased and hence the layers of the thin film are further

grown. This growth results the grains to get larger as observed in this figure. Rutile structures exhibit higher values of nanoparticle size than those of mixed-phase structures, which in turn contain of larger particles when compared to the anatase structures. This is attributed to the thermally-induced growth of grains in the deposited films.

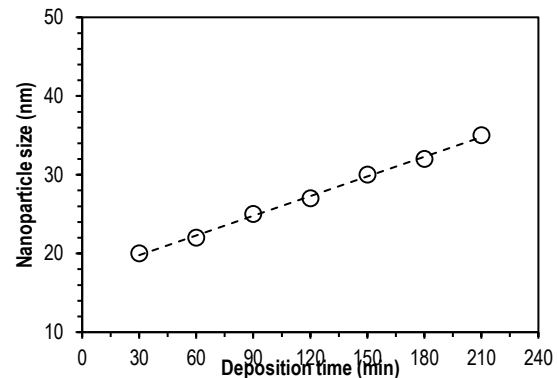


Fig. 12) Variation of nanoparticle size with deposition time for the three types of zinc oxide nanostructures prepared in this work

As the nanopowders were extracted from the thin film samples using the conjunctional freezing-assisted ultrasonic extraction method, the effect of freezing temperature on the value of ultrasonic frequency at which the nanopowder was completely extracted is shown in Fig. (2). As the freezing temperature is decreased, lower frequency is required to extract the nanopowder because lower freezing temperature lead to further shrinkage of the nonmetallic substrate and hence the adhesion of the film to the substrate gets lower.

It is clear that the values of ultrasonic frequencies required for the extraction of nanopowders are relatively convergent regardless the grown phase of zinc oxide, however, the rutile samples needed for higher frequencies due to the thermal effect leading to better adhesion between the film and the substrate.

The variation of nanoparticle size with the ultrasonic frequency at which the nanopowder was extracted for the three types of zinc oxide structures prepared in this work is shown in Fig. (3). As the thin film is typically composed of at least several

layers of zinc oxide particles, higher ultrasonic frequency can vibrate atoms in different layers and hence extract larger particles.

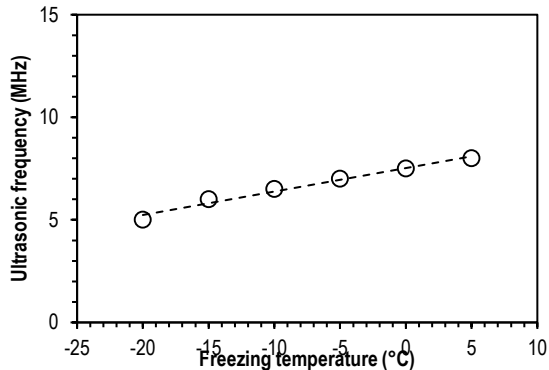


Fig. (2) Variation of ultrasonic frequency with freezing temperature for the three types of zinc oxide nanostructures prepared in this work

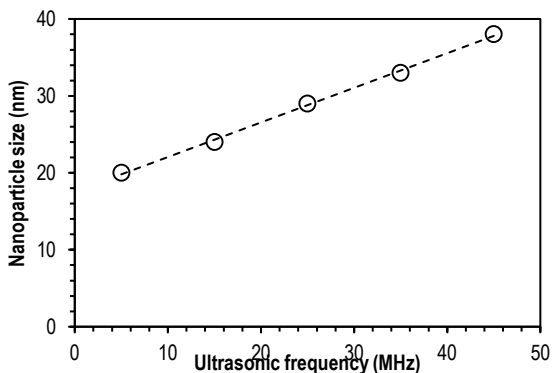


Fig. (3) Variation of nanoparticle size with the ultrasonic frequency for the three types of zinc oxide nanostructures prepared in this work

The time taken to apply the ultrasonic waves to the thin films sample before the extraction of nanopowder was completed is an effective parameter. Accordingly, the variation of nanoparticle size with application time at frequency of 5 MHz is shown in Fig. (4) for zinc oxide thin films. It is clearly observed that the particle size of the extracted nanopowder does not show large differences for application times from 30 to 210 minutes. This is attributed to the fact that particles of certain size are extracted by ultrasonic waves of given frequency regardless the application time. Extraction of particles containing molecules from different layers within the thin film is carried out at certain range of sizes as a function of ultrasonic frequency.

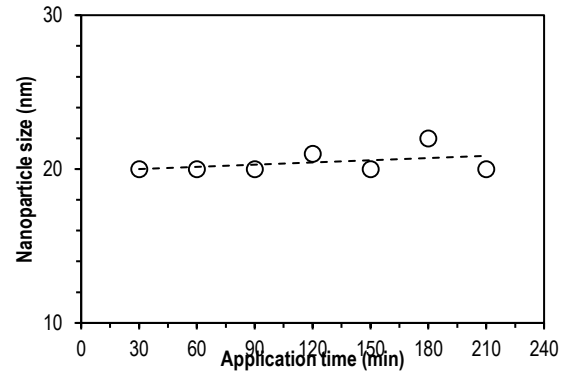


Fig. (4) Variation of nanoparticle size with the application time of ultrasonic waves for the three types of zinc oxide nanostructures prepared in this work

As the extraction method mainly depends on the freezing stage, the freezing temperature may be very effective in determining the particle size of the extracted nanopowder. Figure (5) shows the variation of nanoparticle size with freezing temperature for the zinc oxide samples prepared in this work.

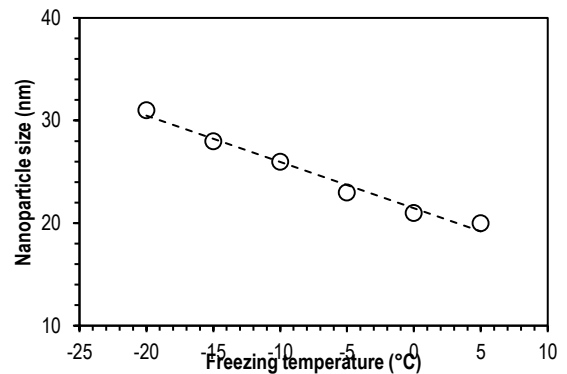


Fig. (5) Variation of nanoparticle size with the freezing temperature for the three types of zinc oxide nanostructures prepared in this work

It was mentioned before that the lower freezing temperature leads to larger shrinkage in the substrate on which the thin film is deposited and hence the adhesion between the film and the substrate gets lower and the film surface breaks earlier at the same value of ultrasonic frequency. Accordingly, larger particles can be extracted from the thin film before partitioning into smaller ones. In contrast, freezing to relatively higher temperatures leads to smaller shrinkage in the substrate and the adhesion between the film and the substrate gets higher. Therefore, the

application of ultrasonic waves can extract zinc oxide particles from the upper surface layer of the thin film, which means smaller particles. Layer-by-layer extraction at higher freezing temperatures produces smaller nanoparticles when compared to the case of lower temperatures.

4. Conclusions

As conclusions, freezing temperature, ultrasonic frequency and the time taken to apply ultrasonic waves on nanostructured thin films deposited on nonmetallic substrates are very effective to determine the nanoparticle size of nanopowders extracted from these thin film samples. The conjunctive freezing-assisted ultrasonic extraction method can be successfully used to extract highly-pure nanoparticles with approximately the same size of nanoparticles in the thin films deposited by physical vapor deposition methods and techniques. This technique is reliable, efficient and low cost to produce highly-pure nanomaterials with as low as possible particle sizes.

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