

Role of the vacuum pressure and temperature in the shape of metal Zn nanoparticles

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Abstract. Zinc (Zn) nanoparticles were fabricated by the high-vacuum thermal evaporation technique. The vacuum pressure was modified from 10^{-6} to 15 Torr and the substrate temperature was increased from room temperature to 100°C in order to evaluate the changes in the morphological and structural characteristics of the Zn nanoparticles. Well-faceted hexagonal disk shaped nanoparticles were formed at a vacuum pressure of 10^{-6} Torr with the substrate kept at room temperature. Aggregation and surface irregularities at the edges of the hexagonal nanodisks were observed with further increases in the vacuum pressure. The nanoscale characteristics of the nanodisks were lost at a vacuum pressure of 10^{-6} Torr and heating the substrate at 100°C . The nanodisks were transformed into Zn wires at a vacuum pressure of 15 Torr with a substrate temperature of 100°C . It is suggested that the initial stages of the growth of the Zn wires are governed by the agglomeration of the Zn nanodisks since the structure of the wires was observed to be composed by stacked nanodisks.

Keywords. Zn; nanodisk; nanowire; vacuum pressure; evaporation.

1. Introduction

Historically, zinc (Zn) has been successfully employed as building block for fabrication of batteries,¹ anticorrosion coatings² and structural alloys.³ Metallic Zn has a low melting point of 419°C and a hexagonal crystal structure with lattice constants of $a = 0.2665$ and $c = 0.4947$.⁴ Most reports on electronic applications related to elemental Zn have been focused on the generation of semiconductor compounds such as CdZnTe,⁵ ZnSe,⁶ TeZn⁷ and ZnO.⁸ In recent times, Zn nanowires have been fabricated with the aim that the one-dimensional effects should improve the superconducting coherence length of Zn, which is almost an order larger than those of other metals.⁹

In addition to Zn nanowires, Zn nanoplates or nanosheets^{10,11} have also been prepared for fabrication of flat nanostructures, which are important for several technological

applications.^{12–15} Zn nanostructures have been prepared by electrochemical methods,⁹ thermal reduction of ZnO¹⁶ and thermal evaporation.¹⁰ Among them, thermal evaporation is a simple method in which a material is heated to the point of evaporation and then is deposited on a substrate surface. In deposition by thermal evaporation, the substrate temperature and the vacuum pressure have proven to be the main experimental parameters in determining the shape of the deposited nanostructure.¹⁷ Although this technique has been successfully used in the preparation of Zn nanowires or nanodisks, the control over the morphology of the synthesized products remains as a challenge. For example, in vapour-phase transport processes, it has been found that in similar growth conditions, Zn nanowires¹⁸ or Zn nanosheets¹⁹ have been collected on the inner walls of a quartz tube. In the present work, Zn nanodisks and wires were deposited by thermal evaporation using different vacuum pressures and temperatures. It was found that the substrate temperature favours the formation of curved Zn wires, which are composed by stacks of Zn nanodisks.

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Table 1. Experimental parameters used for deposition of Zn nanoparticles by thermal evaporation.

Sample	Vacuum pressure (Torr)	Substrate temperature (°C)	Deposition time (h)	Morphology of the Zn structures	Mean size (nm)
1	10^{-6}	Room temperature	1	Well-faceted hexagonal disk	300
2	10^{-6}	100	1	Well-faceted hexagonal disk	1400
3	10^{-4}	Room temperature	1	Irregular-faceted disk	950
4	15	Room temperature	1	Aggregates of Zn disks	600
5	15	100	1	Wires	1000

2. Materials and methods

Zn nanoparticles were prepared by the thermal evaporation technique in a high-vacuum resistive evaporation deposition system (Intercovamex TE12). Aluminium foils (20×20 mm) were used as substrates and fixed on a substrate holder about 30 cm above a molybdenum boat filled with 50 mg of pure Zn shavings (99.99%). Once the vacuum pressure of the chamber was pumped to 2×10^{-6} , 2×10^{-4} or 15 Torr, the molybdenum boat was heated by raising the electrical current with a rate of 3.3 A min^{-1} , reaching a current of 124 A and holding it there for 60 min, with no carrier gas introduced. The substrate was kept at room temperature. Further experiments at 10^{-6} and 15 Torr, at 100°C were performed to evaluate the effect of heating the substrate on the morphology of the Zn nanodisks. Table 1 summarizes the experimental parameters used for deposition of Zn nanoparticles. After the synthesis of the Zn nanoparticles, the chamber was naturally cooled down to room temperature. The products were characterized by field-emission scanning electron microscope (FESEM, JEOL JSM-6510LV) with an acceleration voltage of 20 kV. The structural analysis was carried out using a high-resolution transmission electron microscope (HRTEM, JEM-2200FS) with an acceleration voltage of 200 kV, and an X-ray diffractometer (XRD, Bruker D8 Advances) with a radiation of $\text{CuK}\alpha$ (1.541 \AA).

3. Results and discussion

Figure 1 shows the XRD patterns for the products deposited at vacuum pressures in the range of 10^{-6} –15 Torr, in which the substrate was kept at room temperature. The peaks for all samples were indexed to the hexagonal close-packed Zn structure (space group $P63/mmc$; JCPDS no. 04-0831), without the presence of ZnO peaks, which suggest that the products were not oxidized during the synthesis, even for those deposited at 15 Torr. It is observed a strong (002) preferred orientation in the pattern of the sample deposited at 10^{-6} Torr, which has been associated to the high surface area of Zn nanoparticles.¹⁰ The use of vacuum pressures of 10^{-4} and 15 Torr leads to the gradual reduction in the intensity of the (002) peak, suggesting that the size of the nanoparticles increases simultaneously with the vacuum pressure.

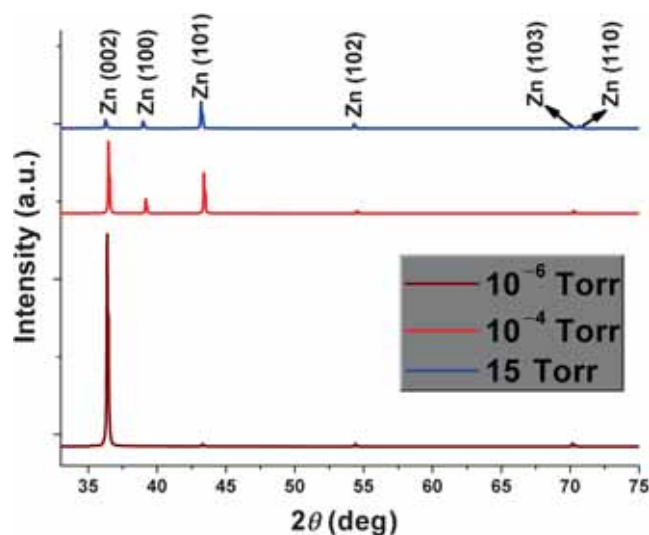


Figure 1. XRD pattern of the Zn nanodisks synthesized by the thermal evaporation technique in the vacuum pressure range of 10^{-6} –15 Torr.

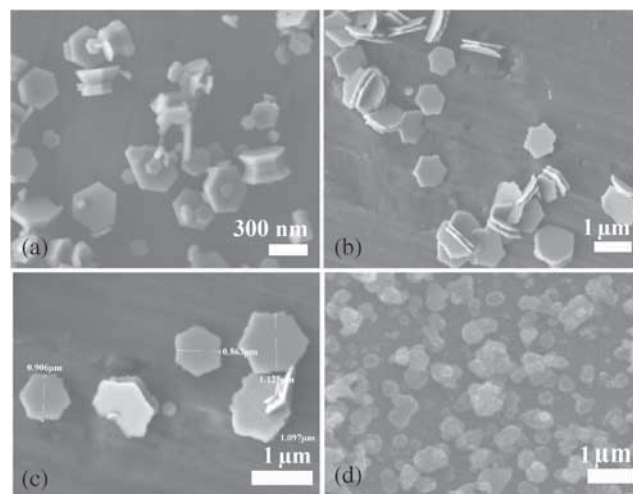


Figure 2. SEM images of the Zn nanodisks deposited by thermal evaporation at different vacuum pressures with the substrate kept at room temperature: (a) 10^{-6} , (b) and (c) 10^{-4} and (d) 15 Torr.

The morphology of the products deposited at vacuum pressures in the range of 10^{-6} –15 Torr with the substrate kept at room temperature is shown in figure 2. Figure 2a shows the

SEM image of the Zn products synthesized at a pressure of 10^{-6} Torr. Well-faceted hexagonal Zn nanodisks with sizes in the range of 100–500 nm and thicknesses between 100 and 200 nm can be observed. No other morphologies were found, which suggest that only one growth mechanism was involved in the formation of the Zn nanodisks. Aggregates of Zn nanodisks with different sizes were also found, which could be evidence of vapour phase reactions.²⁰ The pressure into the chamber was increased in order to evaluate the effect of the vacuum level in the morphological characteristics of the Zn nanodisks. In figure 2b, it is observed that Zn particles with sizes larger than those deposited at 10^{-6} Torr, were formed at a vacuum pressure of 10^{-4} Torr. This image also shows that the smooth shape was lost and surface irregularities at the edges of the Zn nanodisks were formed. The mean size of the Zn nanodisks is found above 800 nm (figure 2c). No significant changes are observed with further increase in the pressure to 15 Torr. The morphology is composed by agglomerates of Zn nanodisks with sizes under 1 μm (figure 2d). Although the smooth surface of the hexagonal nanodisks deposited at 10^{-6} Torr is destroyed with increases in the vacuum pressure, it seems that not exceed 1 μm in particle size even for the sample deposited at 15 Torr.

Unlike other nanostructured materials, metal Zn develops into two main morphologies: Zn nanodisks or nanowires. With the aim to determine the experimental conditions that benefits the growth of Zn nanowires, the substrate was heated at 100°C with two different vacuum pressures: 10^{-6} and 15 Torr (figure 3). In figure 3a, it is observed the SEM image of the sample deposited at 10^{-6} Torr with the substrate temperature kept at 100°C . The morphology is composed by well-faceted hexagonal Zn disks. However, the mean size of the disks is found above 1 μm and their thicknesses above 500 nm, which in contrast with the nanodisks deposited at room temperature shows evidence that the nanoscale characteristics of the Zn nanodisks were lost by heating the

substrate. The Zn nanodisks were transformed into Zn wires with serpentine geometries and irregular surfaces by using a vacuum pressure of 15 Torr and a substrate temperature of 100°C (figure 3b). The morphology observed in figure 3b has been previously reported by other workers.^{18,21,22} The FESEM image of figure 3b shown in figure 3c, shows that the structure of the Zn wires is formed by Zn nanoparticles. High-magnification FESEM image in figure 3d exhibits that the Zn nanodisks merged with each other to develop into Zn wires.

Since the best definition in the morphological characteristics for the Zn particles was observed at the higher vacuum level with a pressure of 10^{-6} Torr, and by considering that disk-shaped particles were found in all samples, the structure of the Zn nanodisks deposited at a pressure of 10^{-6} Torr was also characterized by HRTEM (figure 4). The dark-field image (figure 4a) confirms that the nanodisks have a hexagonal shape with a 120° angle between each pair of adjacent edges. The different contrast observed along the side facets of the particle suggests that hexagonal nanodisks with low thickness attach over each other during the growth process. This oriented attachment is energetically favoured because bonding between nanodisks reduces the overall energy by removing the surface energy associated with dangling bonds.²³

The HRTEM image shows one corner of a single nanodisk (figure 4b). The lattice fringes in some zones are not perfectly aligned, suggesting that the stacked Zn nanodisks are slightly rotated. Analysis of the selected area diffraction (SAED) pattern (inset of figure 4b) confirms that the Zn nanodisk exhibits a single crystalline nature. The SAED pattern is composed of two sets of spots, the outer one (marked by the red arrow) corresponds to a lattice space of 0.24 nm, matching well with the (002) planes of Zn. The inner spots (marked by the white arrow) correspond to a measured lattice space of 0.28 nm consistent with the distance of (100) planes of ZnO. The alignment of both set of spots suggests an epitaxial relationship between the two lattice systems. As metallic Zn is reactive, a thin ZnO layer could be formed on the surface of some Zn nanodisks upon exposure to the

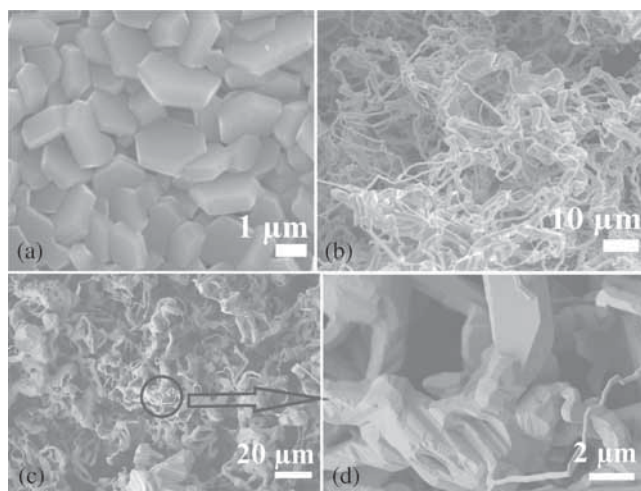


Figure 3. SEM images of the Zn nanodisks deposited by thermal evaporation at (a) 10^{-6} and (b–d) 15 Torr. The substrate was heated at 100°C .

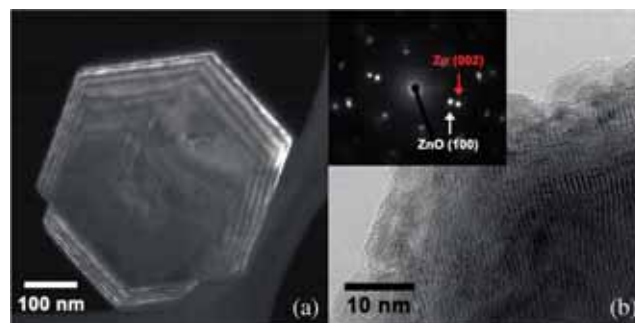


Figure 4. TEM images of a single hexagonal Zn nanodisk deposited at a vacuum pressure of 10^{-6} Torr: (a) dark-field image, (b) high-resolution TEM image from one vertex of the hexagonal structure. The inset shows the corresponding SAED pattern.

atmosphere, although deeper atomic layers are still in the elemental form.

It is known that in vapour synthesis, the competition of the capture of impinging molecules by different surface planes under certain supersaturation conditions determines the final morphology of the nanostructure. The degree of supersaturation of a solute A in air at a temperature T can be calculated by the saturation ratio (S), described by the following equation:

$$S = \frac{P_A}{P_A^s(T)} \quad (1)$$

where P_A is the partial pressure of A and P_A^s the saturation vapour pressure of A in equilibrium with its liquid phase at the temperature of the substrate T . A low degree of supersaturation ($S > 1$), may benefits the growth of 1D nanostructures such as nanowires, nanotubes, nanobelts, among others. A high degree of supersaturation ($S \gg 1$), favours spontaneous nucleation in the gas phase and nanostructures macroscopically seen as powders could be formed.²⁴ As can be seen in equation (1), both pressure and temperature can be controlled to determine the degree of saturation. From the triple phase equilibrium diagram of Zn, solid Zn begins to evaporate at temperatures at of 343°C and pressures below 10^{-2} Torr.²⁵ In similar experimental conditions where a low degree of supersaturation can be assumed, some workers have synthesized pure Zn nanowires.^{26,27} In thermal evaporation processes where the source of evaporation is placed away from the substrate, supersaturation conditions are usually controlled by the temperature gradient in the reaction furnace.²⁸ The difference of temperatures between the evaporation zone and the substrate creates two saturation zones: one is a isothermal zone in the vicinity of the metal evaporation region, and the other one is a supersaturated vapour zone in which the temperature decreases along the distance from the evaporation zone.²⁹ In our experiments, a high degree of supersaturation could be produced near the substrate since vapour pressure of Zn was higher than the partial pressure of Zn, even in the experiment performed at 15 Torr. Although the growth mechanism for disk- and wire-like Zn nanostructures has been independently studied, the presence of Zn nanodisks in the structure of the Zn wires suggest that initial stages of the wire growth includes the Zn nanodisk formation and that the wire growth could be favoured by the substrate temperature. Since the substrate temperature was kept below the melting point of Zn in all experiments and that the process can be considered to be catalyst-free, the growth of wire- and disk-like Zn nanostructures should follows a vapour–solid mechanism. Thus, the growth mechanism for the Zn nanodisks is proposed as follows:

The evaporated Zn atoms reach supersaturation in the gas phase near the substrate. These atoms condense to form Zn nuclei (also called seeds), and then grown into stable nuclei with further addition of Zn atoms. The hexagonal shape developed by the nanodisks can be explained on the basis of the anisotropic growth of the Zn crystal.

The total surface energy during nanocrystals growth is reduced by exposing surface planes that have low surface free energy, which for Zn is the {0001} facet. The planes with higher surface energy grow faster than other planes to minimize the surface energy.

Thus, it is expected that the side facets of Zn are most favoured to the minimization of the total surface energy and hexagonal disks with a narrow distribution of thickness (100–150 nm) were formed.

The SEM image in figure 2a showed that the aggregation of the Zn nanodisks occurred mainly between tiny and big nanoparticles. However, in the TEM image (figure 4a), all stacked Zn nanodisks were observed to have comparable sizes. This difference could be explained by considering that in some cases the small Zn nuclei coalesce into bigger ones via oriented attachment,³⁰ which is seen in the final morphology as assembly of Zn nanodisks with identical sizes. Moreover, it has been suggested that the formation of Zn nanodisks is related to surface processes, which includes formation of liquid droplets of Zn in substrate temperatures about the melting point of Zn (419°C).¹⁰ However, temperatures around 100°C and above could promote the aggregation of the Zn nanodisks and subsequently cause coalescence and growth of longitudinal arrays of stacked Zn nanodisks, which can be seen as curved nanowires.

4. Conclusions

The effect of the vacuum pressure and temperature on the morphological characteristics of Zn nanoparticles was studied. It was found that the size and morphology of the Zn nanoparticles can be controlled by varying experimental parameters such as vacuum pressure and temperature. Zn nanodisks with well-defined geometry can be formed by using a vacuum pressure of 10^{-6} Torr with the substrate kept at room temperature. The increase in pressure and temperature lead to the formation of micrometre Zn nanodisks or their transformation into wire-like-shaped structures.

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