



Controlled growth of zinc oxide nanorods synthesised by the hydrothermal method



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ABSTRACT

Using scanning electron microscopy, atomic force microscopy and X-ray diffraction, we investigated the morphology of ZnO (zinc oxide) films deposited via magnetron sputtering as a function of the chamber's operating pressure. We also studied how ZnO films, when used as templates, influence the morphology of zinc oxide nanorods (ZnO NRs) grown using the hydrothermal method. Our work shows that the resultant ZnO NRs were strongly affected by the initial ZnO film parameters (nanoparticle (NP) distribution and diameter) and, as a result, it was possible to tailor the final ZnO NR morphology by choosing the appropriate template and synthesis conditions. In particular, we showed that, using the hydrothermal method described here, the final ZnO NR mean diameter increased by ~20 nm from the value of the mean diameter of the NPs composing the starting ZnO template film.

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1. Introduction

Zinc oxide (ZnO) is a wide band-gap (3.37 eV) II–VI semiconductor. It is inexpensive, relatively abundant, chemically stable and non-toxic. It has attracted intensive research effort due to its unique properties and versatile applications such as transparent electronics, ultraviolet light emitters, piezoelectric devices, chemical sensors, invisible thin film transistors and spin electronics [1,2]. Throughout the years considerable research has been devoted to the development of methods able to synthesise well-ordered and aligned ZnO nanorods (NRs). These include vapour–liquid–solid [3,4], electrochemical deposition [5], metal–organic chemical vapour deposition (CVD) [6,7] and hydrothermal methods [8]. Among all, the hydrothermal method has been found to be the simplest and the most economical for large scale production of ZnO NRs, although the so grown NRs present lower quality than those prepared by other methods such as CVD [9]. Today one of the key challenges for device application of ZnO NRs is controlling their density. It is well reported that ZnO films serve as the nucleation site for the growth of the ZnO NRs, and the ability to control the morphology of the ZnO films enables the controlling of the orientation and position of the final ZnO NRs. In hydrothermal methods, conventional lithography [10] and shadow masking techniques [11] have been used to control the position and density of ZnO NR arrays by controlling the nucleation sites. However, the issue of controlling the individual rod location and diameter still remains a problem, especially in hydrothermally grown ZnO NRs. The influence of the template growth parameters such as substrate

pre-treatment, precursor's concentration, solution pH and oxygen partial pressures has been investigated [12–14]. Nandi et al. [15] has recently shown that a change of the conventional ZnO film buffer layer to GaN, due to the small lattice mismatch, results in an increase of the resultant nanorod diameter range by a factor of 4, proving this change as ineffective in controlling the individual ZnO nanorods parameters.

In this work we used direct current magnetron sputtering to deposit different ZnO films. These films were then used as templates for the synthesis of ZnO NRs, grown using the hydrothermal method. Using scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray diffraction (XRD), we investigated the influence of the magnetron sputtering chamber's operating pressure on the deposited film's morphology. Our results show that the morphology of the ZnO films is strongly influenced by the deposition pressure and all films present nanostructured morphologies. In addition the film morphology influences the density of the ZnO NRs grown by the hydrothermal method. The resultant nanorods were highly dense with non-uniform dimensions due to the different grain sizes within the individual film samples. Generally we found that, in our experimental conditions, the final ZnO NR mean diameter increased by ~20 nm from the value of the mean diameter of the NPs composing the starting ZnO template film.

2. Experimental procedure

2.1. Deposition of ZnO films by sputtering

ZnO template films were prepared on Si (100) substrates by direct current magnetron sputtering at room temperature using a Zn target

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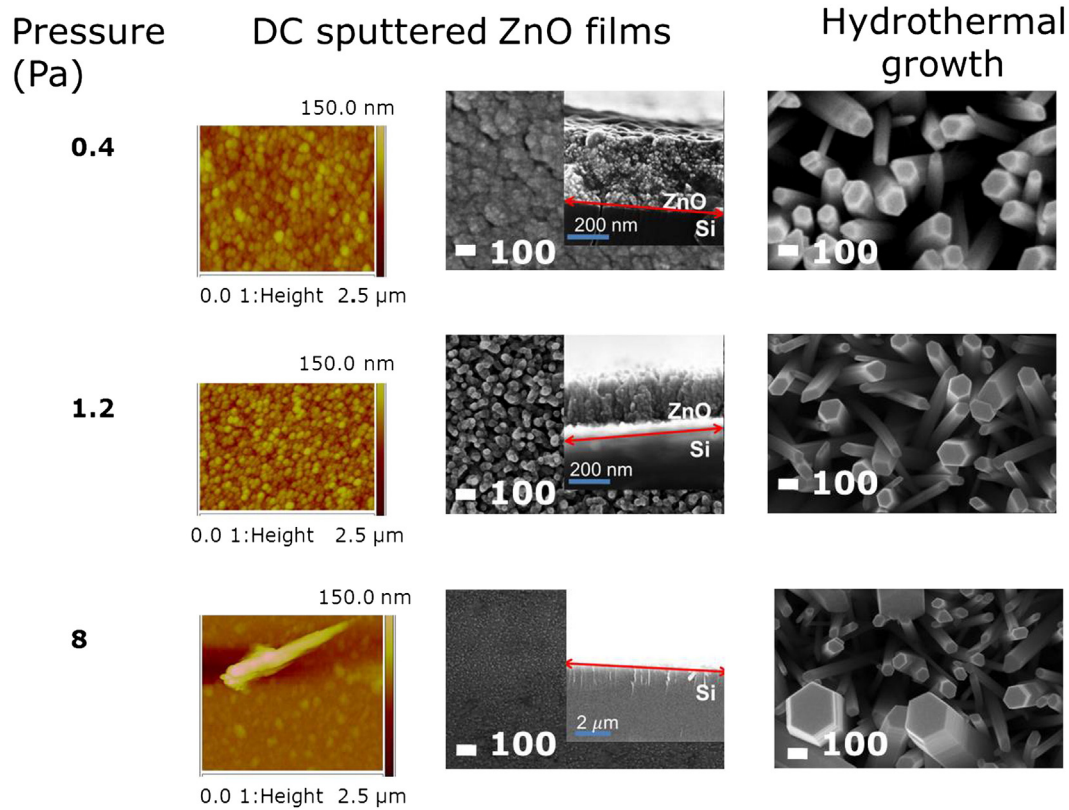


Fig. 1. AFM images (first column from the left) and SEM micrographs (second column from the left) of ZnO films deposited at 0.4, 1.2 and 8 Pa with their respective ZnO NR (third column from the left) SEM images. The SEM images shown in the insets of the second column have been acquired in cross section.

of 99.995% purity and an Orion-5 Sputtering System. The diameter of the Zn target was 50.8 mm and the target to substrate distance was 34 mm. Before deposition the Si substrates were chemically cleaned by ultra-sonication for 10 min in each of the following chemicals: methanol, acetone and distilled water. The silicon substrates also underwent a further cleaning procedure in the sputtering vacuum chamber (base pressure: ~ 0.06 Pa), by exposure to Ar and O₂ gases at the total pressure of 4 Pa for 2 min. During the sputtering process, oxygen was used as a reactive gas to oxidise the deposited metallic Zn target to form ZnO and Ar as the process gas, using a constant oxygen to argon gas ratio of 2:8. Before deposition, the Zn target was pre-sputtered in an Ar atmosphere for 2 min to remove surface contaminants. The sputtering power was kept constant at 60 W for 15 min for all depositions while the total chamber pressure was varied between 0.4, 1.2 and 8 Pa. After deposition the samples were annealed at 400 °C, in situ, for 2 h at an oxygen pressure of 0.4 Pa to further oxidise the film and to form ZnO NPs.

2.2. Synthesis of ZnO NRs via the hydrothermal method

ZnO NRs were synthesised on the ZnO film templates using the hydrothermal method developed by Wang et al. [8]. A solution of zinc chloride (ZnCl₂) with a concentration of 0.05 M was prepared in a bottle with an autoclave cap, using deionised water as a solvent. Aqueous

ammonia (28% w/w) was added to the ZnCl₂ solution while stirring until the pH was approximately 11. The Si/ZnO film was immersed vertically into the prepared solution to synthesize the ZnO NRs. The precursor solution containing the Si/ZnO film was then heated at 90 °C for 60 min. After the deposition the samples were removed from the oven and the solution, and cleaned with deionised water to remove salts or any other contaminant precipitated during synthesis. The samples were then air dried and characterized using SEM, AFM and XRD without further purification.

2.3. Characterization

The AFM topography images of the thin films were obtained using a DI Nanoscope V SPM control station in the tapping mode. The XRD pattern showing the films crystal structure was recorded using a Bruker AXS D8 Advance X-ray diffractometer with a Cu K_α ($\lambda = 0.154$ nm) monochromated radiation source and a position sensitive detector. The analyses were done at iThemba laboratory for accelerator based sciences, Cape Town.

The SEM images were obtained using a SUPRA 35-G34 en 01 apparatus at the Istituto Officina dei Materiali-CNR Laboratorio, Trieste and a Leo-Stereo Scan 440 at the University of Kwa-Zulu Natal, Durban. The SEMs were operated at an acceleration voltage of between 5 and 15 keV.

3. Results and discussion

3.1. Deposition of ZnO template films

Fig. 1 displays the AFM (first column from the left) and SEM images (second column from the left) of the ZnO template films deposited by magnetron sputtering at different chamber pressures. The films were deposited at 0.4, 1.2 and 8 Pa, as shown from top to bottom, with their respective ZnO NRs on the far right, grown using the hydrothermal

Table 1

Summary of the AFM and SEM structural analysis of the ZnO template films. The last column, on the far right, is the diameter of the resultant NRs obtained after the hydrothermal process.

Deposition pressure (Pa)	Film thickness (nm)	NP ave. diameter (nm)	NR ave. diameter (nm)
0.4	350	51 ± 8	70.6 ± 4.1
1.2	250	44 ± 10	62.7 ± 4.5
8	<10	21 ± 3	44.7 ± 3.6

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