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# Surface characterization of ZnO nanorods grown by chemical bath deposition

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## ABSTRACT

The surface composition of as-grown and annealed ZnO nanorods (ZNs) grown by a two-step chemical bath deposition method is investigated by the following surface-sensitive techniques: Time-of-Flight Secondary Ion Mass Spectroscopy (TOF-SIMS), X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES). The presence of H on the surface and throughout the entire thickness of ZNs is confirmed by TOF-SIMS. Based on TOF-SIMS results, the O2 XPS peak mostly observable at  $\sim 531.5$  is assigned to O bound to H. Furthermore, it is found that the near surface region of as-grown ZNs is Zn-rich, and annealing at high temperature ( $\sim 850$  °C) removes H-related defects from the surface of ZNs and affect the balance of zinc and oxygen concentrations.

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## 1. Introduction

Zinc oxide (ZnO) with its interesting properties, such as a large direct band gap and stable exciton even above room temperature (binding energy of 60 meV), has gained substantial interest in the research community [1–7]. Specifically, a growing interest exists in quasi-one-dimensional ZnO nanostructures (e.g. nanorods, nanowires, nanobelts and nanotubes), considered as potential candidates for applications such as gas sensors [1], biosensors [2–3], nanolasers [4], optical waveguides [5–6], and light emitting diodes [4,7]. However, nanostructured materials have a large surface-to-volume ratio compared to epilayer material, which amplifies surface related effects in many ways [1–7]. For optoelectronic applications such as light emitting diodes and solar cells, surface states in the band gap can lead to technical challenges. These states are mostly due to non-stoichiometry, adsorbed foreign species and intrinsic defects in the near-surface region of ZnO. For example, the incorporation of H in ZnO has been shown by cathodoluminescence spectroscopy to strongly affect the green luminescence in ZnO, and indeed in different ways, depending on deviations from the ideal stoichiometry [8]. Bai et al. [9] reported

also that the high surface coverage by the OH-group can affect strongly the sensitivity of ZnO sensors. Yang et al. [10], based on XPS investigations, showed a correlation between surface recombination and the presence of OH-bonds and chemisorbed oxygen on the surface of solution-grown ZnO nanorod arrays, as well as H-bonds on (0001) surfaces. Therefore, it is important to investigate the complete chemical composition and distribution of impurities in ZnO, the surface stoichiometry and to identify the chemical origin and nature of surface recombination centers in ZnO nanostructures [11–16].

In this work, we report surface-sensitive experimental results for solution-grown ZnO nanorods (ZNs). On the one hand, the chemical composition as function of depth was studied by Time-of-Flight Secondary Ion Mass Spectroscopy (TOF-SIMS). On the other hand, X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES) were used to investigate the stoichiometry of the ZnO nanorod surfaces as function of annealing temperature.

## 2. Experimental details

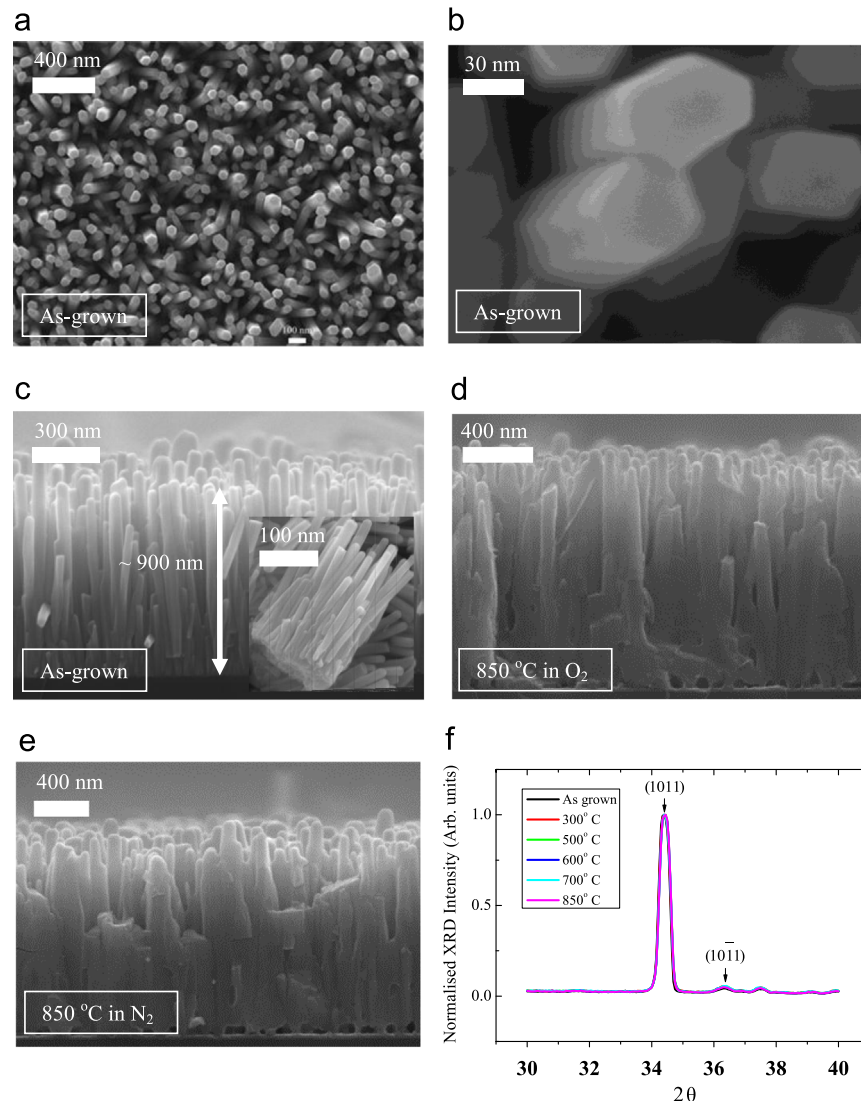
The ZNs used in this investigation were grown on Si substrate by chemical bath deposition (CBD) as reported recently by Urgessa

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et al. [14]. Two steps were followed: firstly the deposition of a ZnO seed layer on a cleaned silicon substrate (001), and secondly the growth of ZNs on the pre-treated substrate at 85 °C in an aqueous mixture of zinc nitrate hexahydrate and hexamine (pH 5.5). Before the deposition of the seed layer, the substrate was cleaned sequentially using trichloroethylene (TCE), acetone, methanol, and de-ionized (DI) water and blown dry in nitrogen gas. A well agitated ethanolic solution made of 5 mM of zinc acetate dihydrate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ) and 0.0101 g of polyvinylpyrrolidone (PVP) was spun five times onto the pre-cleaned substrate using a spin coater. Then the spin coated substrate was annealed in an oxygen environment for 30 min at 300 °C at atmospheric pressure. This spin coating and annealing process was repeated twice. For the formation of the nanorods, the seeded substrate was immersed into the growth solution, which was a mixture of aqueous solutions of zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3 \cdot 6\text{H}_2\text{O})$ ) and hexamethylenetetramine (hexamine) ( $\text{C}_6\text{H}_{12}\text{N}_4$ ). After growth, ZN samples were cleaned with deionised water and blown dry by nitrogen gas. For further treatment and different investigations, the dried sample was cleaved into several pieces and kept in clean non-sealed containers. Annealing experiments were conducted in a horizontal quartz tube at 300 °C, 400 °C, 500 °C, 600 °C and 850 °C in controlled flows of  $\text{N}_2$  and  $\text{O}_2$  for 30 min.

A field emission scanning electron microscope (SEM) (JEOL 7001F FESEM) was used to investigate the morphologies of the nanostructures. The crystalline nature of the nanostructures was confirmed using a Bruker D8 Discover X-ray Diffractometer with a  $\text{Cu-K}\alpha$  X-ray source ( $\lambda = 1.5405 \text{ \AA}$ ). A detailed description of the TOF-SIMS system is given elsewhere [15]. It is worth noting that depth profile investigations were done in ultra-high vacuum of  $\sim 10^{-8}$  mbar for positive ion spectroscopy and  $\sim 10^{-9}$  mbar for negative ion spectroscopy. Only an area of  $100 \times 100 \mu\text{m}^2$  was analyzed from a  $300 \times 300 \mu\text{m}^2$  sputtered area, in order to avoid edge effects. Sputtering was done in the positive mode by an oxygen gun (1 keV, 250 nA) and in the negative mode by a cesium gun (2 keV, 130 nA). Detailed surface analysis was done by a PHI 5000 Versaprobe-Scanning ESCA Microprobe (XPS) [17] and a PHI 700 Scanning Auger Nanoprobe. The excitation beam for XPS and AES measurements was  $\sim 100 \mu\text{m}$  and  $\sim 10 \text{ nm}$  in diameter, respectively. Sputtering during XPS and AES experiments was performed with an Ar ion gun at a rate of  $\sim 18 \text{ nm/min}$  and  $\sim 22 \text{ nm/min}$ , respectively. The energy resolution of both systems is 0.5 eV and the margin for error of the detector of photoelectrons and Auger electrons, are 2% and 5%, respectively. XPS and AES experiments were done at  $4 \times 10^{-9}$  Torr and  $2.85 \times 10^{-10}$  Torr, respectively.



**Fig. 1.** (a–c) Typical top view and cross sectional SEM micrographs of the as-grown ZNs. (d, e) Typical cross sectional SEM micrograph of ZNs annealed at 850 °C for 30 min respectively in  $\text{O}_2$  and  $\text{N}_2$ . (f) Normalized XRD spectra of as-grown ZNs and oxygen-annealed samples.

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