Effect of the gas composition on the structural and electrical properties of ZnO nanostructures obtained by oxidation of Zn at atmospheric pressure

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Abstract. In this work we report the synthesis of ZnO nanorods on glass substrates by a simple thermal evaporation of high purity Zn powder without the use of any catalyst. The product was obtained at atmospheric pressure by the oxidation of Zn vapour in a flow of Ar and O₂ gas mixture at low temperature of glass substrates (390 °C). The morphology, phase composition and crystallinity of the nanostructures were investigated by scanning electron microscopy and X-ray diffraction analysis. Their electrical properties were studied via current-voltage (I-V) measurements. XRD demonstrates that the nanorods deposited consist predominantly of the wurtzite phase of ZnO with preferred c-axis orientation. The results show that the oxygen content in the deposition atmosphere influences strongly the morphology and electrical resistance of the produced ZnO nanostructures.

1. Introduction
In the area of nanomaterial research, one-dimensional nanoscale semiconductors have attracted lots of interest due to their promising applications in electronics, photonics, sensors, transducers, energy generation, and so on [1-5]. The properties and performances of these new nanomaterials are mainly controlled by their nature, size and morphology, which in turn determine their electrical conductivity, optical absorption, UV and visible light emission or chemical reactivity [4]. The tendency of ZnO to grow in a variety of exotic morphologies has induced great interest to explore simple methodologies to grow such nanoarchitectures. After publication by Yang and co-workers of their seminal paper on synthesis of ZnO nanowires [6], many methods have been developed to produce ZnO nanostructures such as vapor phase methods (thermal evaporation and condensation, metalorganic chemical vapor deposition), solution phase method, etc. (for reviews see [1, 7, 8] and references cited there in). Different types of ZnO nano- and microstructures were reported in the literature, synthesized by the thermal evaporation processes using metallic zinc powder as source materials for zinc. ZnO micro and nanorods were synthesized on silicon substrates in a horizontal quartz furnace by the thermal evaporation of metal zinc powder under oxygen ambient [9, 10]. Vertically aligned ZnO nanowires were prepared through vaporization of metal zinc powder at low temperature using the Au-coated silicon substrates [11]. In all of the results presented previously, the scientists used either metal catalysts or crystalline substrates for the growth of ZnO nanostructures.

In this paper, we report the synthesis of ZnO nanorods on glass substrates at relatively low temperature (390 °C) without use of any metal catalyst or seeds, via a simple thermal evaporation of
zinc powder at atmospheric pressure. The influence of the oxygen content in deposition atmosphere on the texture, crystallinity, grain size, morphology and electrical resistance of the nanostructured layers obtained has been studied.

2. Experimental

ZnO nanostructures were grown on glass substrates using a metal vapour deposition method. The schematic diagram of the experimental setup for the fabrication of ZnO nanostructures is shown in Figure 1. Zinc powder (99.9999 %) was placed in a quartz boat as the Zn source in the center of a quartz tube in a furnace. The quartz tube was kept at atmospheric pressure by flowing high purity Ar (99.99%) with a flow rate of 300 sccm and heated up to 710 °C. Ar carrier gas with different O₂ content varying from 2 to 20 vol. % flows through the quartz tube with the rate of 500 sccm at reaching the synthesis temperature. All gas flows were controlled by mass flow meters controllers. The growth time was set to 30 min before terminating oxygen flow and cooling down to room temperature.

The layers were deposited on glass substrates, carefully cleaned. The cleaning procedure first involved washing with a 1% detergent solution and then with deionized water in an ultrasonic cleaner. The substrates were placed horizontally at the downstream side of the Zn source at a distance of about 25 cm. The temperature of the substrate, controlled by a thermocouple, was 390 °C. The thickness of the layers of about 500 nm was measured by a profilometer type Talystep.

![Figure 1. Schematic diagram of the experimental setup for the fabrication of different shape ZnO nanostructures.](image)

The crystal structure of the layers was characterized by X-ray diffraction (XRD), using a Philips (PW 1710) apparatus with Cu-Kα radiation separated by a graphite focusing monochromator. Smoothing processes of 5 point Fast Fourier transform followed by an appropriate baseline correction were applied to all diffraction spectra. The intensity and full width at half maximum (FWHM) of an (hkl) plane were determined by profile fitting procedure, using an Gaussian or pseudo Voigt peak shape after Kα2 stripping procedure.

The surface morphology of the layers was examined by a scanning electron microscope (SEM Philips 515). The resistivity measurements were provided with 2 mm planar narrow strip Al electrodes, 200 nm thick, with a distance of 2.9 mm between each other. They were vacuum deposited through a precise stainless steel mask on the free ZnO surface. Current – voltage (I-V) measurements were performed in dark at 25 °C with Keithley 230 voltage source and Keithley 617 electrometer.

3. Results and Discussion

The layers deposited were white in color. The phase of the layers and their crystallographic orientation were determined by XRD spectra. XRD pattern of the layers deposited on glass plates at indicated O₂ content in Ar/O₂ gas mixture during their deposition are given in Figure 2. The XRD results show that the ZnO layers are polycrystalline. Five peaks observed at 31.55, 34.2, 36.0, 47.30 and 56.4° match the values given in powder diffraction file 05-0664 [12] while the relative intensities of these peaks are
distinct from those of ZnO powder. These peaks can be indexed to (100), (002), (101), (102) and (110) planes of the hexagonal wurtzite structure of ZnO crystal.

![XRD patterns of the layers deposited on glass plates at indicated O2 content in Ar/O2 gas mixture.](image)

**Figure 2.** XRD patterns of the layers deposited on glass plates at indicated O2 content in Ar/O2 gas mixture.

In order to quantify the preferred orientation (PO), often called texture, in the crystalline films, the texture coefficient ($T_c$) was defined as [13]

$$T_c(hkl) = \frac{I(hkl) / I_o(hkl)}{N^{-1} \sum_n I(hkl) / I_o(hkl)}$$

where $I(hkl)$ is the measured intensities of a (hkl) plane converted into the corresponding intensity of an infinitely thick sample, $I_o(hkl)$ is the intensity of a random oriented ZnO powder standard measured at the same conditions, $N$ is the reflection number and $n$ is the number of the diffraction peaks. A sample with randomly oriented crystallites presents $T_c(hkl) = 1$, while the larger the value, the larger the abundance of crystallites oriented at the (hkl) direction.

The average grain size ($D$) of crystallites was calculated using well-known Scherrer’s formula [14]:

$$D = \frac{0.9 \lambda}{\beta \cos(\theta)}$$

where $\lambda$ is the wavelength of X-rays used (=1.54059 Å), $\beta$ - the broadening of diffraction line measured at half its maximum intensity in radians and $\theta$ - the angle of diffraction in degree.

![Texture coefficient $T_c$ (a) and grain size $D$ (b) calculated from XRD patterns of the (100), (002) and (101) peaks in dependence of O2 content in the gas mixture.](image)

**Figure 3.** Texture coefficient $T_c$ (a) and grain size $D$ (b) calculated from XRD patterns of the (100), (002) and (101) peaks in dependence of O2 content in the gas mixture.
Figure 3 presents the influence of the oxygen content in deposition atmosphere on $T_c$ and average grain size calculated by from XRD patterns of the (100), (002) and (101) peaks. The higher value of $T_c$ obtained for (002) peak than the other ones is an indication of preferable c-axis phase with good crystalline quality formed on pure glass substrates. As a whole, the increasing O$_2$ content above 10% degrades c-axes PO and leads finally to more random orientation with lower crystalline quality. It is seen that the average grain size of c-phase also decreases since the growth of the grain along substrate surface is enhanced.

Figure 4 shows SEM images of the layers grown on pure glass substrates at different oxygen content in carrier gas. It is seen that the layers deposited at O$_2$ content up to 10 % in the gas mixture consist of ZnO nanorods grown perpendicular to the substrate surface. ZnO nanorods were produced regularly on a whole substrate (30 mm x 20 mm). All the observed nanorods exhibit hexagonal surfaces throughout their length with hexagonal facets. The average diameter of grown nanorods increases with the O$_2$ content, which is consistent with the data by XRD analysis. A further increase in the amount of oxidizing agent in the carrier gas destroys the uniformity of the layer. The substrate is covered with small drops consisting of randomly distributed ZnO nanowires shown in the figure.

The XRD and SEM analyses shed some light on the growth mechanism. The formation of ZnO nanostructures with different morphologies is obviously due to the different O vapor pressure since the morphologies of ZnO layers are mainly influenced by the concentration of oxygen gas. Most probably the growth of ZnO nanorods and nanowires followed a self-seeding vapor–solid (VS) growth mechanism [7]. In the initial growth stage, the self-seeding occurred on the glass substrate and then the ZnO nanorods grew on the seeds by feeding with the evaporated zinc and oxygen elements. In addition, with a sufficient supply of oxygen sources, some ZnO seeds grow laterally on the substrate.
with formation of nanowires. Further study however, is needed for understanding the exact nuclei and growth mechanism.

![Graph](image)

**Figure 5.** (a) I-V characteristics of ZnO layers obtained at indicated O₂ content; (b) Resistivity (ρ) of the ZnO layers in function of O₂ content in the gas mixture.

Figure 5a depicts the current–voltage (I–V) characteristics measured between pairs of the fabricated ohmic contacts. They clearly show an ohmic behaviour which implies good quality ohmic contacts and that the ZnO layer is conducting. Figure 5b plots the resistivity of layers in dependence of the O₂ content in the gas mixture. It is seen that the resistivity of ZnO nanostructures increases from $7.2 \times 10^6 \Omega \text{cm}$ to $1.2 \times 10^9 \Omega \text{cm}$ as the oxygen content in carrier gas increases from 2.5 to 20 %. This result is in correspondence with the data of other authors published in the literature [15].

As it was well known undoped ZnO thin films have n-type conduction which is caused by a deviation from stoichiometry due to native defects. Various kind of native point defects are present in ZnO layers [15]. They include oxygen vacancies (V\textsubscript{O}), zinc vacancies (V\textsubscript{Zn}), Zn interstitials (Zn\textsubscript{i}), oxygen interstitials (O\textsubscript{i}), Zn atoms at oxygen anti-sites (ZnO), and oxygen atoms at Zn anti-sites (O\textsubscript{Zn}). Previously, (V\textsubscript{O}) and Zn\textsubscript{i} have been assumed to be the main sites of donors in ZnO crystals. However, recent first principles calculations verified that V\textsubscript{O} is a deep donor and it cannot be the origin of n-type conduction [16]. In contrast, Zn\textsubscript{i} can act as a shallow donor. The high value of ρ of about $1.2 \times 10^9 \Omega \text{cm}$ obtained for ZnO layers deposited at high O₂ content in gas mixture indicates that the number of defects in ZnO layers have diminished. More probably in our case with the increase in oxygen content in the gas mixture during the deposition some oxygen vacancies and especially interstitial Zn disappear thus causing the increase in film resistivity.

4. Conclusion

The polycrystalline nanostructured ZnO layers consisting of nanorods and nanowires were obtained at low temperature of glass substrates without the use of any catalyst or seeds at atmospheric pressure. The XRD data indicate that the nanorods exhibit the hexagonal wurtzite structure with preferred c-axis orientation. The crystallinity, texture and the grain size of the deposited nanostructures depend on the oxygen content in the carrier gas. The high O₂ content degrades c-axes phases and leads finally to phases with lower crystal quality and more random orientation. The results by I-V measurements show that the resistivity of the nanostructures increases with increasing amount of oxidizing agent in the gas.

It can be expected that due to their characteristics these nanostructured layers may be used as building blocks for preparing chemical and biosensors as well as photocatalysts where inherently large surface to volume ratio of structured materials are important prerequisite for enhanced sensitivity.
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