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Growth of ZnO nanorods by air annealing of ZnO films with an applied electric field

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Abstract

A novel method of ZnO nanorods growth is presented based on low temperature (300 °C) air annealing of ZnO film while applying an electric field (~10 V/cm) parallel to the film. The films were deposited on glass substrates using a filtered vacuum arc deposition system equipped with a Zn cathode, at an arc current of 160 A, oxygen pressure of 3.2 mTorr, and deposition time of 30 s. Cu tape electrodes were applied on each end of the coated sample, and used to apply the electric field. The samples were annealed in a quartz furnace at 200, 300, 400 °C for 20 or 60 min. Each sample surface was examined using a Scanning Electron Microscope (SEM) and a High Resolution SEM (HRSEM) to study its micro- and nano-structure. The film crystallographic structure was studied using X-ray diffractometry (XRD). ZnO rods with lengths of ~3 μm were observed on the samples annealed at 300 °C for 20 min with an electric field of ~10^3 V/m, while separated conical forms with lengths of ~0.5 μm and base width of ~150 nm were observed after annealing under the same conditions but without any electric field. The rod growth rate and area density were ~2.0–2.5 nm/s, and ~3×10^7 cm^{-2}, respectively.

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1. Introduction

One-dimensional semiconductors are considered as important components in future nanometer-scale optoelectronic devices, e.g. electrically driven, single-nanowire lasers [1], and room temperature ultraviolet laser arrays of from vertically aligned zinc oxide (ZnO) nanorods [2]. ZnO nanorods are of special interest due to their high exciton binding energy of 60 meV, which is significantly larger than other materials commonly used for blue-green light-emitting devices. Gas sensors based on ZnO nanorods would have high sensitivity due to their high surface-to-volume ratio.

The ability to synthesize nanorods at arbitrary locations at moderate temperatures is needed for nanodevice integration. The development of simple and low cost methods that could be applied at relatively lower temperature and without catalyst is an actual and important research objective. Several techniques have been developed for the fabrication of various ZnO nanostructures, e.g. nanowires and nanorods. These techniques are based on catalyst assisted vapor phase transport [2], metalorganic vapor-phase epitaxy [3,4], vapor–liquid–solid (VLS) process [5], or the porous template method [6,7]. Site-selective nucleation and growth of ZnO nanorods were achieved by a high-temperature vapor transport process catalyzed by Au [2], and by molecular beam epitaxy onto Ag island catalysts on Si substrates [4]. In the last case, the typical growth time was 2 h with growth temperatures ranging from 300 to 500 °C. A dense entangled collection of ZnO nanorods was observed to grow from the surface. Both cylindrical nanorods and faceted whiskers were observed in forest of ZnO nanostructures grown at 400 °C. At higher temperatures, only

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nanorods were observed. In many cases, the length of ZnO nanorods was in excess of 2 μm. Multiple nanorods were observed to nucleate from the relatively large Ag islands.

In most reports on ZnO nanorods or nanowires growth, a vapor–liquid–solid (VLS) process with gold (Au) nanoparticle catalysts was used [5]. However, there are some apparent drawbacks in the VLS growth technique. It requires a very high growth temperature, up to 925 °C, so that Zn vapor can be dissolved into an Au catalyst to form an alloy droplet. After saturation, Zn precipitates out from the droplet and is oxidized to form ZnO nanorods. Vertical ZnO nanorods were grown without a catalyst on sapphire substrates by plasma-enhanced chemical vapor deposition, during 1 hour heating in a gas mixture at 700 °C [8]. However, the growth of ZnO nanorods on ZnO film without any catalyst and at relatively low temperature (~200–400 °C), and with applied electric field has not been previously reported. Each of the reported techniques have some specific deficiencies, such as the use of high temperature, the need for a catalyst, a relatively long production period, the need for special substrates, environmental problems, or high costs.

The objective of the present work was to determine the effect of annealing and the simultaneous application of a parallel electric field on the structure of ZnO thin films. The ZnO films were grown on glass substrates by filtered vacuum arc deposition. Film morphology and structure were analyzed by high resolution microscopy and X-ray diffractometry (XRD). ZnO nanorods were observed only on annealed samples on which an electric field was simultaneously applied.

2. Experimental details

Thin films of zinc oxide were deposited on a (26×2 mm) area of a glass substrate in a filtered vacuum arc deposition (FVAD) system. A 160 A arc was sustained between a Zn cathode and a Cu anode in a 3.2 mTorr oxygen atmosphere, and the deposition time was 30 s. The films were approximately 150 nm thick, and had an as-deposited resistivity on the order of 0.1 Ω cm. The initial characteristics before annealing were the same for all samples. The basic scheme of the experimental set-up for the film processing is shown in Fig. 1. Cu tape was applied at each end of the sample to serve as electrical connectors for measuring the resistivity and for the application of a d.c. electric field parallel to the film during annealing. The field was uniform on the sample, except very near to the edge (~1 mm from the edge), as was determined by measuring the equipotential lines. The deposited samples were attached to a boron nitride holder and annealed in an atmospheric air ambient in a cylindrical quartz tube furnace at 200, 300, 400 °C (the controlled temperature fluctuated ±3 °C around the preset temperature) for a duration of 20 or 60 min. Every experiment was thrice repeated with new samples for each time.

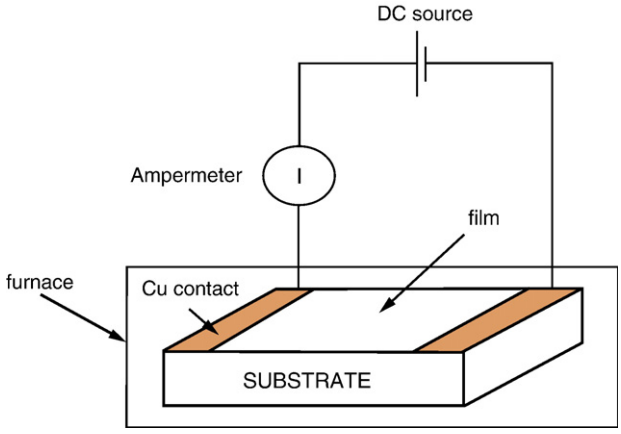

Fig. 1. The basic scheme of the experimental set-up.

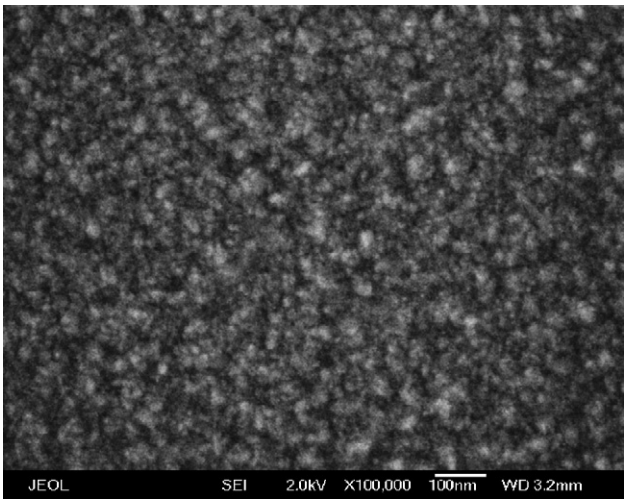

Fig. 2. High resolution SEM micrograph of ZnO film before annealing.

The film surface was studied using a JSM-6300 Scanning Electron Microscope (SEM) for microstructure, and a JSM-6700F High Resolution SEM (HRSEM) and High Resolution TEM (HRTEM) for nanostructures. Energy dispersive X-ray (EDX) analysis was used to determine the objects composition. The crystallographic structure was studied by using X-ray diffractometry (Bragg–Brentano geometry) and grazing incidence X-ray diffractometry (parallel beam optics)) with a θ–2θ diffractometer (D5000, Siemens), equipped with a special thin film attachment. A sample of the film was scraped off of the substrate and transferred to a grid for HRTEM examination.

3. Results and discussion

A typical HRSEM micrograph of the as-deposited film is shown in Fig. 2. It is seen that the film surface consists of grains with sizes in the range of ~10–30 nm.

The application of the electric field on samples that were not annealed did not affect the surface grain structure.

Three HRSEM of film surface after annealing at 300 °C, with and without the application of an electric field are presented in Fig. 3. Fig 3a shows a HRSEM image of a sample surface annealed without the imposition of an electric field, whereas the effect of the imposition of electrical fields during the annealing is demonstrated in Fig. 3b and c. After annealing, nano-size objects were observed on all film surfaces. Energy dispersive X-ray (EDX) analysis was used to determine the objects composition. The EDX patterns of the objects and of the film area without any nano-objects are shown in Fig. 4a and b