



# Characterization of optoelectronic properties of the ZnO nanorod array using surface photovoltage technique

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## ABSTRACT

Well-aligned ZnO nanorod array, synthesized by wet chemical bath deposition (CBD) method on conductive indium–tin–oxide (ITO) substrate, was characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and photoluminescence (PL) spectroscopy. Surface photovoltage (SPV) technique based on a scanning Kelvin Probe system was employed to investigate the optoelectronic behavior of ZnO nanorod array. The surface photovoltage and its time-resolved evolution process are used to determine the energy level structure of the ZnO nanorod array.

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## 1. Introduction

In recent years, one-dimensional (1D) ZnO nanostructures have attracted increasing interest due to its many exciting properties, such as a wide band gap (3.37 eV), a large exciton binding energy (60 meV), excellent chemical and thermal stability, transparency, and wide electrical conductivity range [1]. Among these 1D ZnO nanostructures, there has been considerable attention focused on single-crystal ZnO nanorod array on account of its potential applications in nano-electronic and optoelectronic devices, such as field-effect transistors [2] and solar cells [3,4]. Characterization of optoelectronic properties like photovoltage behavior in ZnO nanorods is particularly important for the design and fabrication of the devices. The Kelvin Probe technique with its high sensitivity and high spatial resolution provides a well-established contactless and nondestructive method for semiconductor characterization, which relies on the analysis of the photo-induced change in surface voltage [5]. Moreover, the energy levels of semiconductors can be obtained by contact potential measurements [6,7]. This also indicates that the Kelvin Probe technology can be used to monitor the electronic properties at the localized energy levels. As a result, Kelvin Probe (KP) based SPV technique has been widely used as an efficient tool for characterizing the optoelectronic properties of semiconductors [8–10].

The purpose of this work is an attempt to investigate the optoelectronic properties of ZnO nanorod array using a scanning Kelvin Probe system. The surface photovoltage spectrum and its time-resolved evolution process as well as the energy level structure of ZnO nanorod array are also discussed.

## 2. Experimental details

Chemical bath deposition (CBD) technique has been proven to be a good approach for the synthesis of ZnO nanorods with the use of ZnO seeds in the form of thin film or nanoparticles [11]. In this paper, ITO glass was chosen as a substrate for growth of ZnO nanorod array by the CBD technique. The ITO substrate was cleaned in the ultrasonic bath with acetone, ethanol and deionized water to remove adsorbed dust and surface contamination. In order to fabricate vertically aligned nanorods, the ZnO seed layer was first fabricated on the pre-cleaned substrate by radio-frequency (RF) magnetron sputtering. Then the ZnO/ITO substrate was heated to 350 °C in air for 15 min. After cooling, the ZnO seed-coated substrate was vertically put into fresh aqueous solution composed of a 0.05 M zinc acetate dehydrate ( $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ , 98%) and 0.05 M methenamine ( $\text{C}_6\text{H}_{12}\text{N}_4$ , 99%) in the sealed autoclave, which was then placed in a laboratory grade box oven and kept at a constant temperature of 95 °C for 5 h. All the chemical reagents were analytic grade. After ZnO growth, the substrate was taken out of the solution and thoroughly rinsed several times with deionized water, and then blew dried with high pure  $\text{N}_2$  gas at room temperature. The details of chemistry process by CBD technique can also be found elsewhere [12].

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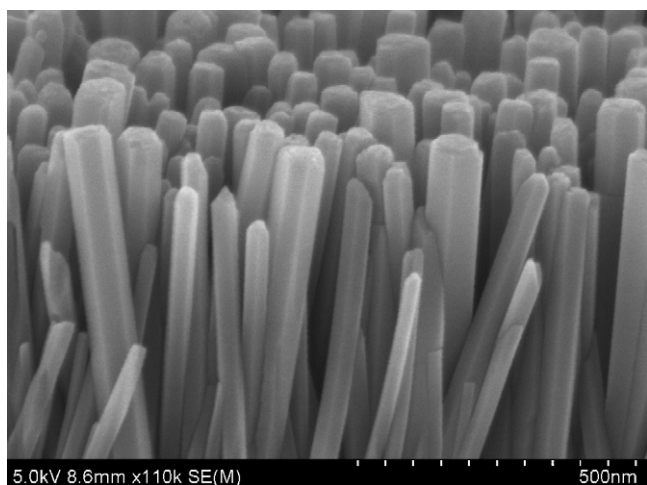


Fig. 1. FESEM image of the ZnO nanorod array sample grown on the ITO substrate.

The morphology and dimension of as-grown ZnO nanorod array were observed by field-emission scanning electron microscopy (FESEM) on HITACHI S-4800. Crystal phase identification of the ZnO nanorod array on the ITO substrate was obtained by X-ray diffraction (XRD) on Bruker Axs D8. To investigate the optical properties, photoluminescence (PL) measurement was performed at room temperature using a He–Cd laser with an excitation wavelength of 325 nm.

Kelvin Probe (KP) based SPV measurements were carried out on a commercial KP system (KP Technology Ltd., England). The Kelvin Probe is a vibrating capacitor device that is used to measure the work function difference between the sample and vibrating tip (gold tip with the work function of 5.1 eV is used in this paper). The diameter of the gold reference probe is 1.8 mm. A 600 W tungsten–halogen lamp and a double-prism monochromator provided the monochromatic light. All the measurements were performed at room temperature.

### 3. Results and discussion

The typical FESEM image of the ZnO nanorod array sample was shown in Fig. 1. It can be clearly seen that an array of highly dense ZnO nanorods is perpendicularly oriented to the substrate and nearly all the ZnO nanorods have well-defined hexagonal prism shape. Furthermore, it shows that each nanorod has a uniform diameter along its entire length, indicating that the growth anisotropy is constantly maintained. The diameter of ZnO nanorods ranges from 40 nm to 100 nm, which indicates the small-sized ZnO nanorods can be successfully obtained by CBD technique.

The X-ray powder diffraction pattern of the as-grown ZnO nanorod array on ITO substrate was shown in Fig. 2. Here, the data showed three major peaks: a strong peak at  $34.4^\circ$  along with two much weaker peaks at  $31.8^\circ$  and  $62.8^\circ$ . The evaluated  $d$ -spacing values of these peaks are nearly matching with the standard JCPDS bulk ZnO data (36–1451) and hence the diffracted peaks are belonging to (002), (100) and (103) orientations, respectively. The intensity of the (002) diffraction peak is far stronger than that of other peaks such as (100) and (103), indicating that most of the ZnO nanorods grow preferentially along the  $c$ -axis direction as hexagonal wurtzite structure and perpendicularly to the substrate surface.

The study of photoluminescence is a favorable way to evaluate both ZnO optical properties and its structure defects. Room-temperature PL spectra of ZnO nanorods grown on ITO substrate, which was recorded using a 325 nm He–Cd laser as the excitation

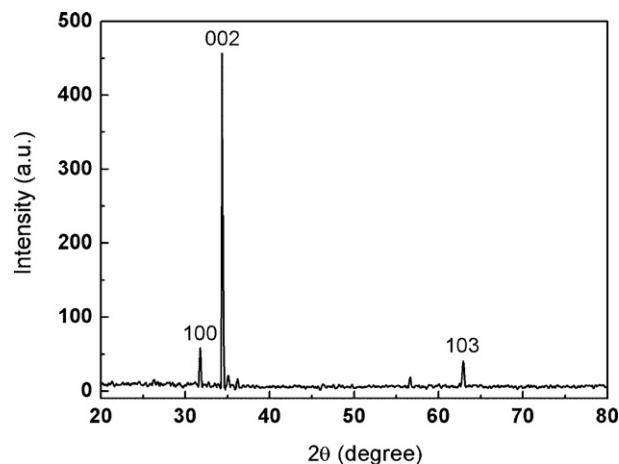


Fig. 2. Typical XRD pattern of the as-grown ZnO nanorod array.

light source, is shown in Fig. 3. The ultraviolet (UV) emission in ZnO PL spectra was well accepted as the near-band-edge emission, which results from the recombination of free excitons [13,14]. On the other hand, the visible emission band in PL spectra was usually observed for most ZnO nanorods reported in the literature, which was believed to be closely related to the defect level induced by the defects of O vacancies, Zn interstitials or their complexes [15,16]. In our case, however, it should be noted that strong UV emission peak centered at wavelength of 379 nm was observed for the ZnO nanorod array on ITO substrate, while the well-known broader emission situated in the yellow–green part of the visible spectrum could not be observed clearly, indicating high optical quality ZnO nanorod array was successfully achieved via this simple process chemical approach at low temperature. This UV emission peak mainly originated from the free carrier or excitonic transition between the valance band and the conduction band at an energy point of  $\sim 3.27$  eV. This value is nearly matching with the optical band gap of ZnO [17]. The full width at half-maximum (FWHM) value of the UV emission is calculated to be 0.19 eV (22 nm). The present sharp excitonic emission implies that the ZnO nanorod array in this work maybe have an excellent UV emission property with a low defect concentration.

Prior to illumination, all the samples were maintained in the dark for an extended period to eliminate persisting effects of previous light exposure. The SPV spectrum was obtained by scanning the wavelength of monochromatic light from visible to UV spectral region with the rate of about 0.5 nm per second. The SPV spectrum

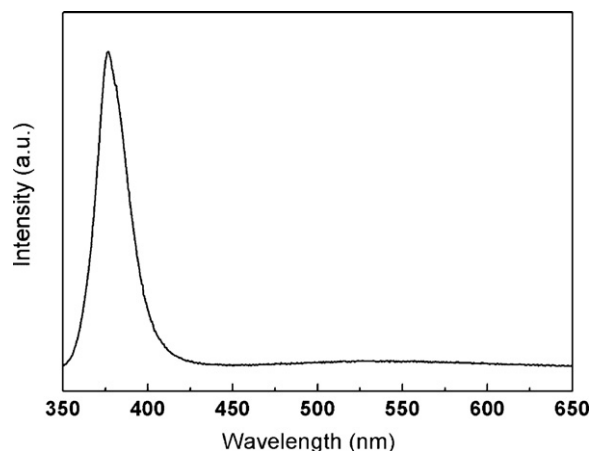


Fig. 3. Photoluminescence spectra of the as-grown ZnO nanorod array.

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