

Field emission properties of aligned ZnO nanorods on Ti substrate

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Abstract. Aligned ZnO nanorods were grown on titanium (Ti) substrate by simple and facile thermal evaporation process using high purity metallic zinc powder in the presence of oxygen. The grown nanorods were studied in terms of their morphological, structural and field emission properties by using different analytical tools such as field emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD). The field emission properties of the as-grown aligned ZnO nanorods were also investigated which resulted in a turn-on field of ~2.65 kV. This research demonstrates that simply prepared ZnO nanorods can be used for field emission device applications.

1. Introduction

Research on 1D semiconductor nanomaterials has received a great deal of attention due to their unique morphologies and wide applications in various high-technological areas including photovoltaics, electronics, sensors and actuators, to name but few such areas [1]. Among the various semiconductor nanomaterials, the II-VI wurtzite hexagonal phase ZnO is particularly interesting due to its own properties and wide applications in various areas of science and technology. Moreover, the 1D nanomaterials of ZnO such as nanorods, nanowires, nanofibers, nanoneedles, etc are very attractive due to their tunable electronic and optoelectronic properties and various high-technological applications, for instance, nanoscale electronic and optoelectronic devices, sensors and actuators, solar cells, nanogenerators, laser operating at room-temperature and so on [2]. Recently, the use of various substrates for the growth of 1D ZnO nanomaterials has received great attention as particular substrates are needed for specific applications. The substrates used for the growth of ZnO nanorods/nanowires are various orientations of silicon chips [3-5], stainless steel grid [6], indium tin oxide substrates [7], nylon fibers [8], alumina [9], anodized aluminum oxide [10], CaF₂ [11], steel alloy substrates [12], and so on.

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In this paper, attempt has been made to grow well-crystalline ZnO nanorods on Ti substrate which were examined in detail in terms of their morphological, structural, and field emission properties. To the best of the author's knowledge, this is the first report in which vertically aligned and well-crystalline hexagonal ZnO nanorods were grown on Ti substrate by facile thermal evaporation of metallic zinc powder in the presence of oxygen at moderate temperatures.

2. Experimental details

For the growth of aligned ZnO nanorods, commercially available high purity (99.9%) Ti substrates were used. Prior to the growth, the substrates were ultrasonically cleaned with DI water, alcohol and acetone, sequentially. The growth of nanorods on several pieces of 1cmx1cm Ti substrates was carried out by a facile thermal evaporation process by using metallic zinc powder in the presence of oxygen. After loading the source materials and substrates, the chamber pressure was evacuated down to 2 mbar using a rotary vacuum pump and the same pressure was maintained during the whole reaction. During the reaction, the furnace was rapidly heated up to 750 °C in the presence of high purity nitrogen (20 sccm) and oxygen (100 sccm) gases. The reaction was completed in 1.5 hr. The furnace was naturally cooled to room-temperature and the deposited structures were analyzed in terms of their morphological and structural properties using a field emission scanning electron microscope (FESEM) and X-ray diffraction (XRD) with Cu-K α radiation. The field emission properties of the grown structures were also investigated.

3. Results and discussion

3.1 Morphological, compositional and structural properties of as-prepared ZnO nanorods on Ti Substrate

The general morphology of the as-deposited ZnO sample on Ti was imaged by field emission scanning electron microscopy (FESEM). Figure 1 (a) exhibits the typical secondary electron (SE) images of the as-synthesized ZnO nanorods on Ti substrate. The SE image reveals that the synthesized nanorods are grown in very high density and vertically aligned to the substrate surface (figure 1 (a)).

To examine the crystallinity and crystal phases, the as-prepared ZnO nanorods were examined by X-ray diffraction (XRD). Figure 1 (b) exhibits the typical XRD pattern of the as-prepared ZnO nanorods. All the observed diffraction reflections in the XRD pattern are well matched with the wurtzite hexagonal phase of pure well-crystalline ZnO and hence confirm that the prepared nanorods are well-crystalline and possessing wurtzite hexagonal phase of ZnO. Some small diffraction reflections at 38.4°, 40.3° and 53.1° are also seen in the observed XRD pattern of ZnO nanorods which are related with the Ti substrate as was confirmed by measuring the XRD pattern of pure Ti substrate.

Figure 1 (c) exhibits the typical low-magnification TEM image of the as-grown ZnO nanorods which shows clean and smooth surfaces and uniform diameter throughout the length of the ZnO nanorod in the range of 15-20nm. The inset of figure 1 (c) shows the corresponding SAED pattern of the nanorod shown in figure 1 (c). The observed SAED pattern shows very well defined, ordered diffraction pattern which confirmed that the grown nanorods are well-crystalline and preferentially grown along the c-axis direction. Figure 1 (d) exhibits the typical HRTEM image of the nanorods shown in figure (c). The HRTEM image shows the well-defined lattice fringes with the inter-planar distance of 0.52 nm, equal to the lattice constant of crystalline ZnO. This fact clearly confirms that the prepared nanorods are well-crystalline ZnO.

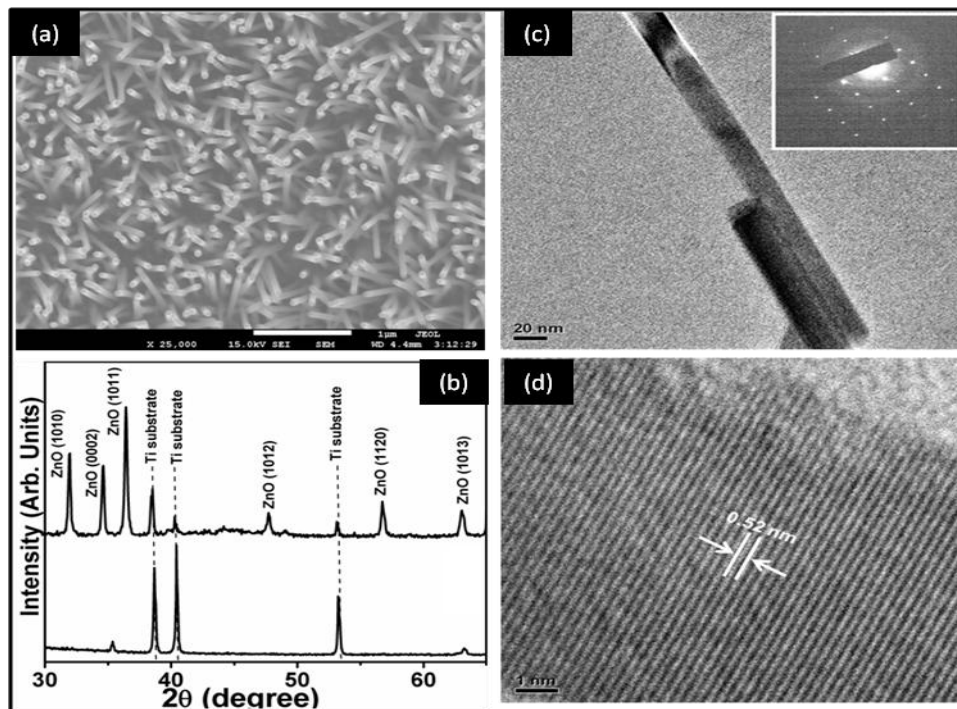


Figure 1. Typical (a) FESEM image, (b) XRD pattern and (c and d) low-magnification and high-magnification TEM images of as-grown ZnO nanorods on Ti substrate and with diameters in the range of 15-20nm.

3.2 Field emission properties of the as-prepared ZnO nanorods on Ti Substrate

The field emission (FE) properties of ZnO nanorods were also investigated using a triode configuration under a base pressure of $\sim 5 \times 10^{-8}$ mbar. For the FE measurements, two experimental scans were carried out for each sample. Figure 2 (a) shows the typical I-V behaviour (measured current as a function of applied voltage) of the ZnO nanorods. It is seen that in the initial scan, referred to as first scan, the emission current increased with increasing the applied voltage. The initial turn-on voltage is 2.55 kV with the observed emission current of ~ 100 nA. A maximum emission current of ~ 13 μ A was recorded at an applied voltage of 4.56 kV. In the first scan, the emission current was quite unstable. Moreover, the I-V curve of the first scan usually appears to be noisy and this is attributed to surface contamination of the emitting sites [13]. Therefore, repeated scans were necessary to achieve stable and reproducible emission current.

A much stable and less noisy I-V curve was obtained in case of the second FE measurement which can be attributed to the removal of the surface's contaminants during first FE scan. However, slightly higher voltage was required for the same emission current. The interpolated value of the turn-on voltage for an emission current ~ 100 nA is ~ 2.65 kV.

The Fowler–Nordheim equation was employed to analyse the behaviour of the emission current versus the applied voltage. The F-N equation can be expressed as

$$J = 1.54 \times 10^{-6} \frac{(\beta E)^2}{\Phi} \exp \left(-6.83 \times 10^9 \frac{\Phi^{2/3}}{\beta E} \right)$$

Where J is the current density, E is the macroscopic value of the applied field ($E = V/d$ where V and d are the applied voltage and the distance between the anode and the sample, respectively). β refers to the field enhancement factor and Φ is the work function which is 5.3 eV for ZnO [14]. Fitting the data using the Fowler–Nordheim (F-N) plots showed linear behaviour indicating that the field emission

process is dominant. The (I-V) characteristics, a representative image of the field emission pattern from the sample and the F-N relationship are shown in figure 2 (a) and (b) respectively.

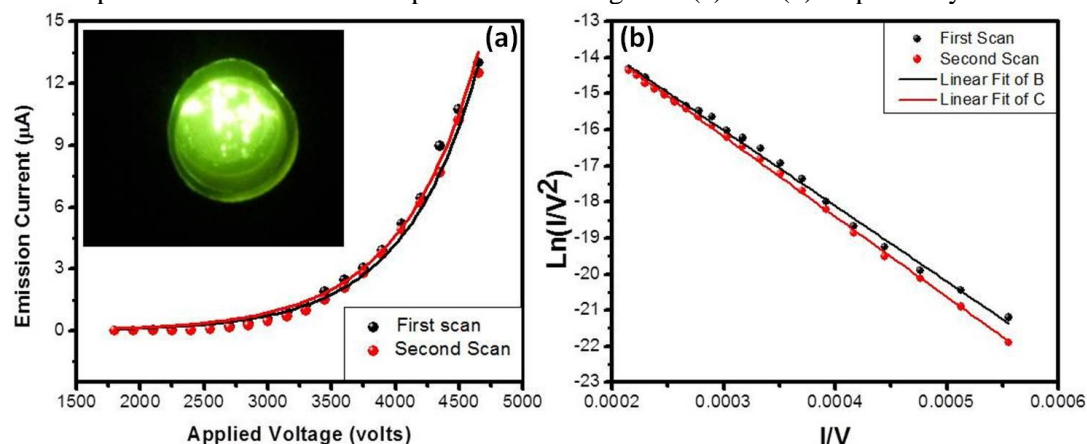


Figure 2. FE measurements of ZnO nanorods; (a) current-voltage curve and the typical FE pattern image (inset of (a)) and (b) corresponding F-N relationship.

4. Conclusion

In summary, a simple and facile approach has been adopted to grow aligned ZnO nanorods on Ti substrate and their morphological, structural and field emission properties have been explored. The detailed morphological and compositional properties of the as-grown products revealed that the prepared nanomaterials are “ZnO nanorods” which are aligned to the substrate surface while the structural studies revealed that the prepared nanorods are well-crystalline and possessing wurtzite hexagonal phase. Finally, the field emission performance of the vertically aligned ZnO nanorods on Ti substrate was investigated and presented in this paper.

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