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Surface structure optimization for cost effective field emission of zinc oxide nanorods on glass substrate

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ABSTRACT

Density and aspect ratio engineering of ZnO growth are very attractive for many applications. In this article, we report the effect of seed layer thickness on the density of zinc oxide (ZnO) nanorod arrays on glass substrate without any conductive electrode in a low temperature (85 °C) chemical bath deposition process. It was demonstrated that when the seed-layer thickness changes from 50 to 200 nm, the nanorod density increases from 7.8×10^6 to 6.5×10^8 cm^{-2}. In addition, this density variation is accompanied by the change of both diameter and height of the nanorods. The results on different nanorad arrays showed that the properties of field emission follow the Fowler–Nordheim law. The variation of the density and the aspect ratio was found to have a serious effect on the field emission characteristics. Finally, an optimal density of $10^7/cm^2$ and aspect ratio of 46.48, demonstrated the best field emission profile. The field emission property of a single ZnO nanorod depends mainly upon their aspect ratio, which is essentially attributed to the change of the field enhancement factor in a single ZnO nanorod.

1. Introduction

Electron sources play a critical role in information displays. They mostly use the thermionic emission mechanism, where electrons are emitted from heated filaments (hot cathodes) [1]. Field emission is an alternative mechanism to extract electrons. In recent years, one-dimensional (1D) semiconducting nanostructures have received tremendous research interest for their potential application in nano-scale electronic and optoelectronic devices such as transistors, light-emitting diodes, photodetectors, and chemical sensors. These 1D nanostructures include nanorods (NRs), nanotubes, nanobelts, and nanoneedles. The small dimensions of these structures result in higher device packaging density, lower power consumption, and also more sensitivity for chemical sensing applications [2]. Zinc oxide (ZnO), As a II–VI compound semiconductor with a wide and direct band gap of 3.37 eV, has been shown to be a prime candidate for the electronic and optoelectronic applications described above. Field emission from zinc oxide (ZnO) nanorods has attracted so much attention in recent years due to their potential application in vacuum micro/nano electronic devices [3–5]. For obtaining an excellent field emission performance from a nanorod array, it is important to find an optimal density of nanorods. While field screening effect from high-density emission sites is poisonous for such a phenomenon, deep understanding of this effect can minimize its consequences. On the other hand, to have electron emission at low field, nanorods having a large aspect ratio are also desirable [6]. Investigation on how to find an optimal density for field emission has been carried out. In the extensively studied vapor–liquid–solid (VLS) method, the ZnO nanorod density can be tuned by controlling either the density of the Au catalyst nanoparticles or the thickness of the Au film [7,8]. For example, Wang et al. [7] demonstrated that the nanorod density decreases from 11.2×10^9 to 1.5×10^9 cm^{-2} when the thickness of the gold film increases from 1 to 8 nm. The best field emission performance from these nanorod arrays was obtained for densities between 6×10^9 and 8×10^9 cm^{-2}. Though the VLS method has good capability of the density control, the high-temperature (>900 °C) growth process is incompatible with the typical fabrication procedure of vacuum micro/nano electronic devices [9]. The synthesis of ZnO nanorods by using the low-temperature solution-phase method provides an alternative way to develop ZnO nanorod-based field electron emission devices [10,11]. As compared to its high-temperature counterparts, the solution-phase method has merits of low temperature, no catalyst, low cost, ease of scale-up, and patterned growth [12].

However, despite strong effort and interest, the development of a facile method for tuning the density in a wide range remains a challenge [13,14]. Meanwhile, the mechanism responsible for the variation of nanorod density by changing the thickness of the seed-layer is not fully clear. More importantly, the effect of the change of the nanorod density on the field emission has not been investigated. It is known that the aspect ratios of the nanorods vary with the density. Therefore, it is difficult to obtain the optimal density and the large aspect ratio simultaneously. As stated at the beginning, the density and the aspect ratio can affect the field emission properties of nanorods. Thus, to perform this study, it is necessary to find an optimal condition of these

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two parameters. Herein, we present results on (i) the effect of the seed layer on ZnO nanorod growth, and (ii) a systematic field emission study to find an optimal condition of the two parameters.

2. Experimental details

This study was performed by changing the thickness of the ZnO seed layers. The ZnO films were deposited using a RF sputtering unit on 1×1.5 cm^2 glass substrates. The seed layer thickness was controlled by the deposition time, i.e., 15, 30 and 60 min. The evaluation of ZnO nanowire has been further carried out by an AFM indentation method. For this purpose, a SOLVER NEXT scanning probe microscope (NT-MDT Co., Zelenograd, Moscow, Russia) was utilized to obtain elasticity and surface topography of ZnO nanowire arrays. X-ray diffraction (XRD) by Philips Xpert MPD diffractometer (40 kV, 40 mA), with Cu-Kα radiation ($\lambda = 0.15418$ nm) measurements were carried out on the seed layers for the purpose of characterizing how the crystal planes are formed in the seed layer and the finally grown nanorods. The samples with ZnO films were then suspended in the nutrient solution for the NR growth. The nutrient solution (200 mL) was a mixture of 0.005 M zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and 0.005 M hexamethylenetetramine (HMTA, $C_6H_{12}N_4$). The growth was performed at 85 °C for 6 h. The samples were then rinsed with deionized water and dried with a nitrogen blower. Field emission scanning electron microscopy (FESEM, HITACHI S-4160, 20 kV) was used to characterize the morphology of the samples. The as-synthesized products were also characterized by transmission electron microscopy (TEM, JEM-2010-JEOL, Japan, 400 kV). The field emission studies were carried out in a chamber having a vacuum of ~1.33 Pa at room temperature. The cathode was the as grown ZnO nanorod and a metal anode with diameter of 5 mm was then placed on top of the sample surface. For the field emission measurement, the separation between the anode and the cathode (nanorod sample) was fixed at 200 μm. For electrical conductivity measurements, another small circular silver paste pad (area = 3.14 mm^2) were formed on the ZnO surface. After evacuating the chamber, an external voltage with ascending magnitude is applied to the anode and the resulting emission current was measured using a Keithley-K361 parameter analyzer. The testing electric field (E) was estimated by dividing the applied voltage (V) by the anode–cathode distance (V/d). The emission current density (J) was calculated from the obtained emission current and the area of the rounded hole in the mica. The emission current–voltage characteristics were analyzed by using the Fowler–Nordheim (FN) equation [15]. The green phosphor-coated indium tin oxide (ITO) glass was used as anode plate, and the emission current was measured at the cathode. The green phosphor was used to record the image of field emission electrons from patterned ZnO nanorod.

2.1. Effects of seed-layer thickness on density, and aspect ratio of the NRs

Fig. 1 shows the AFM surface morphology of the ZnO films with different thicknesses of 50 nm, 100 nm and 200 nm. It indicates that the surface topology strongly depends on the layer thickness, as it is clear from Fig. 1 (a–c). The surface RMS roughness increases from 0.3 to 2.1 nm with thickness increment from 50 to 200 nm (Fig. 1d).

Fig. 2a shows the cross-sectional scanning electron microscopy (SEM) images of the NR arrays grown on the 200 nm seed layer with 6.3 μm thickness and ~150 nm in diameter. Fig. 2b illustrates a TEM

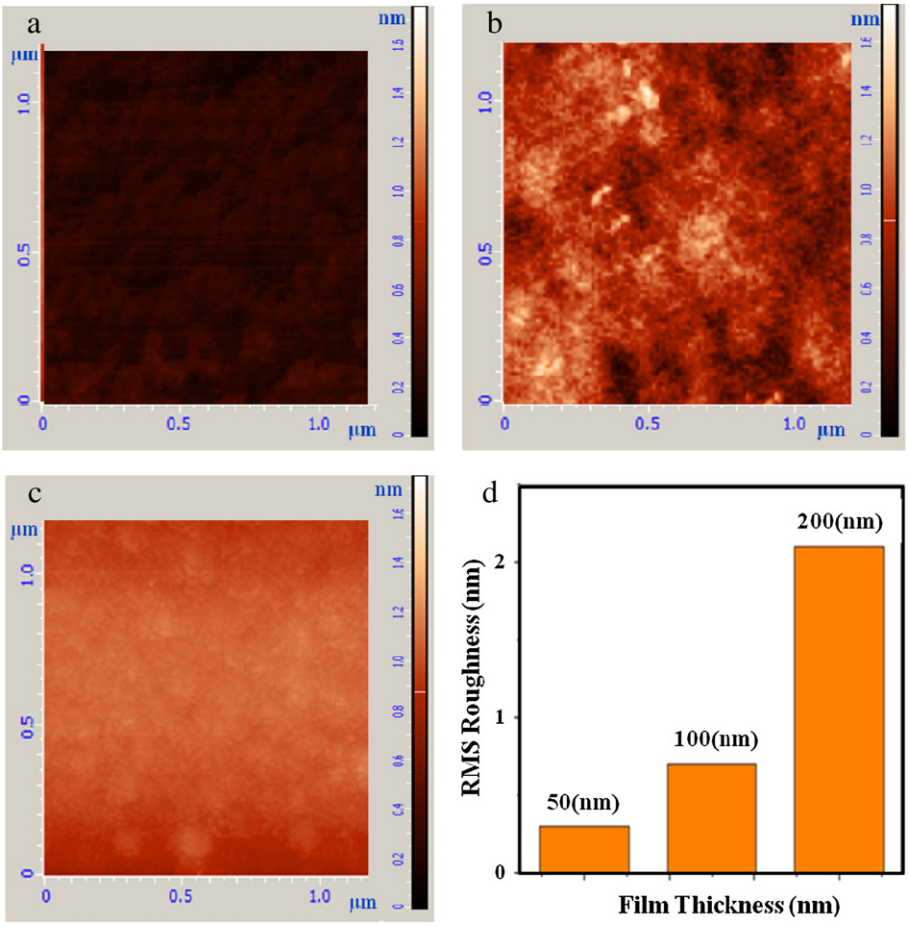

Fig. 1. 1.2 μm × 1.2 μm AFM images of ZnO seed layers with different thicknesses of (a) 50 nm, (b) 100 nm and (c) 200 nm. (d) RMS roughness of the seed layers.