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Array of vertically aligned Al-doped ZnO nanorods: Fabrication process and field emission performance

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ABSTRACT

We report the development of a novel field emission (FE) device based on Al-doped ZnO nanorods (NRs), which can be used as an alternative tool for exhale biosensing applications. Highly crystalline hexagonal array of ZnO NRs doped with up to 5 wt% Al content were obtained using hydrothermal growth method. Field emission process with acceptable enhancement factor ($761 < \beta < 951$) were performed for 1 to 4 wt% Al-doped ZnO nanorod arrays. By increasing the Al content above 5 wt%, the morphology of nanorods started to transform into the nanoplates, demonstrating weak FE performance. When a high voltage was applied to 4 wt% Al-content ZnO NRs for a few times (4–6×), an abnormal microstructure formation with improved FE performance was observed. Significant field emission current with enormous enhancement factor ($\beta = 5545$) was demonstrated from the high Al-content reformed ZnO microstructure assembly. The formation of these microstructures was found to be due to the diffusion and electromigration of Au atoms through the grain boundaries into the NR assembly.

1. Introduction

Field emission mechanism plays a vital role in gas sensing with high sensitivity and accuracy [1]. For the diagnosis of diseases from human respiratory, one needs to detect tiny concentration of specific gases with numerous precision and with low power expenditure [2]. Exponential dependence of current on the applied voltage in field emission mechanism has converted this process to the method of choice with potentially high precision results [3]. High-speed amenability and low power consumption makes the use of field emission more attractive [4]. Turn-on field (E_{t_o}), threshold field (E_{t_h}), emission current density, field screening effect and the field enhancement factor (β) are the figures of merit used for the field emission performance [5]. Zinc oxide (ZnO), with a wide and direct band gap of 3.37 eV and 60 meV exciton binding energy at room temperature, has been shown to be a prime candidate for the nano-scale, one dimensional, low power applications [6,7] with high device packaging density and more chemical sensitivity and stability [7–11]. ZnO has also been introduced to be the material of choice for an effective cathode emitter with high electronic conductivity [5,6,12,13]. In order to achieve an excellent FE performance from a nanorod (NR) array, the array's electronic conductance, reduction of work function through the energy band binding and the metal contact quality are important factors [14]. Aluminum-doping can positively affect the FE properties as one of the most common dopants for ZnO. Al-doping could affect bandgap and the carrier concentration of the ZnO structure [15,16].

In this article, the effect of Al-doping has been examined on the material characteristics of the ZnO NRs array. Interestingly, a new phenomenon has been observed and reported in high Al-doping samples. In order to investigate the field emission improvement in the presence of Al-doping, all devices were measured at comparable conditions in a vacuum chamber and the results were compared.

2. Materials and methods

To investigate the nanorods' field emission property, different weight contents of Al dopant were incorporated into the ZnO NR structures. For this purpose, glass substrates in $6 \times 6\ cm^2$ sizes were initially cleaned by sonicating in acetone, ethanol, and de-ionized (DI) water. The schematic diagram of the fabricated field emission devices is shown in Fig. 1. To stablish the bottom contact to the active part of the device, radio frequency (RF) plasma sputtering was employed to deposit Ti/Au contacts (25/350 nm). The Ti layer was used as an adhesion promoter in between Au and the glass substrate. Next, on top of the Au layer, 200 nm thick 2% Aluminum-doped ZnO (AZO) seed layer was deposited using RF plasma sputtering.

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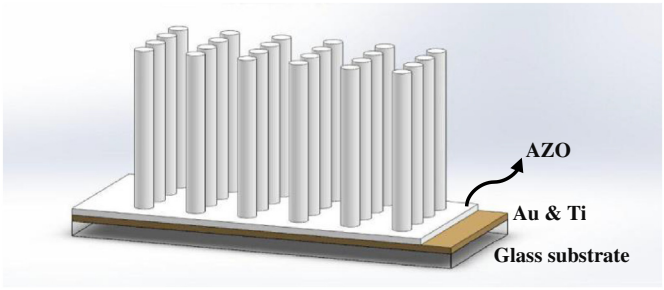

Fig. 1. Schematic of the manufactured devices: ZnO NRs were grown using hydrothermal method.

In order to grow the nanorods using chemical bath deposition [17], the sample was suspended face down in the precursor solution. The precursor solution (100 ml) made up of an equimolar (1:1) of zinc nitrate hexahydrate powder ($Zn(NO_3)_2{\cdot}6H_2O$, Merck, Germany) and hexamethylenetetramine powder (HMTA, $C_6H_{12}N_4$, Merck, Germany). The doping precursor, aluminum nitrate nonahydrate powder ($Al(NO_3)_3{\cdot}9(H_2O)$, Merck, Germany), was added to the solution by varying the weight ratio of Al to Zn between 1 and 7 wt%. The process lasted 6 h at 87 °C. After the growth, nanorods were formed vertically with an average height of 2.9(± 0.2) μm.

The morphology of the grown nanorods was examined using field emission scanning electron microscope (FESEM, HITACHI S-4160). X-ray diffraction (XRD) by Philips X'pert, with Cu-Ka radiation (λ = 0.15418 nm) was used to explore the effect of doping concentration on the crystallinity of ZnO NRs. The as-synthesized products were

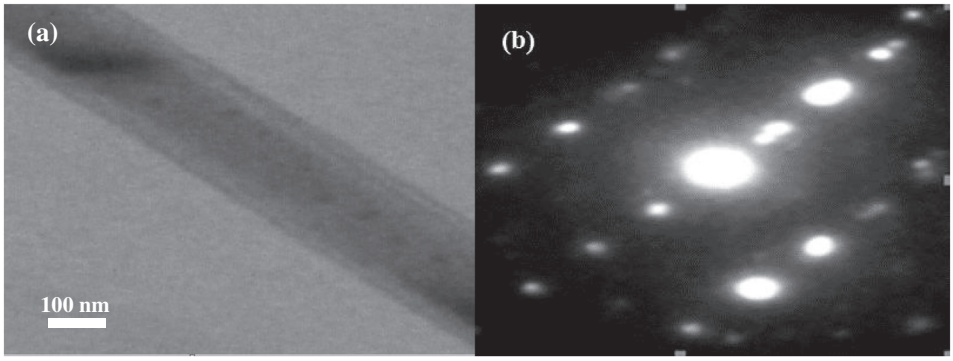

Fig. 2. a) TEM and b) a selected-area electronic diffraction pattern (SAED) of a typical ZnO NR.

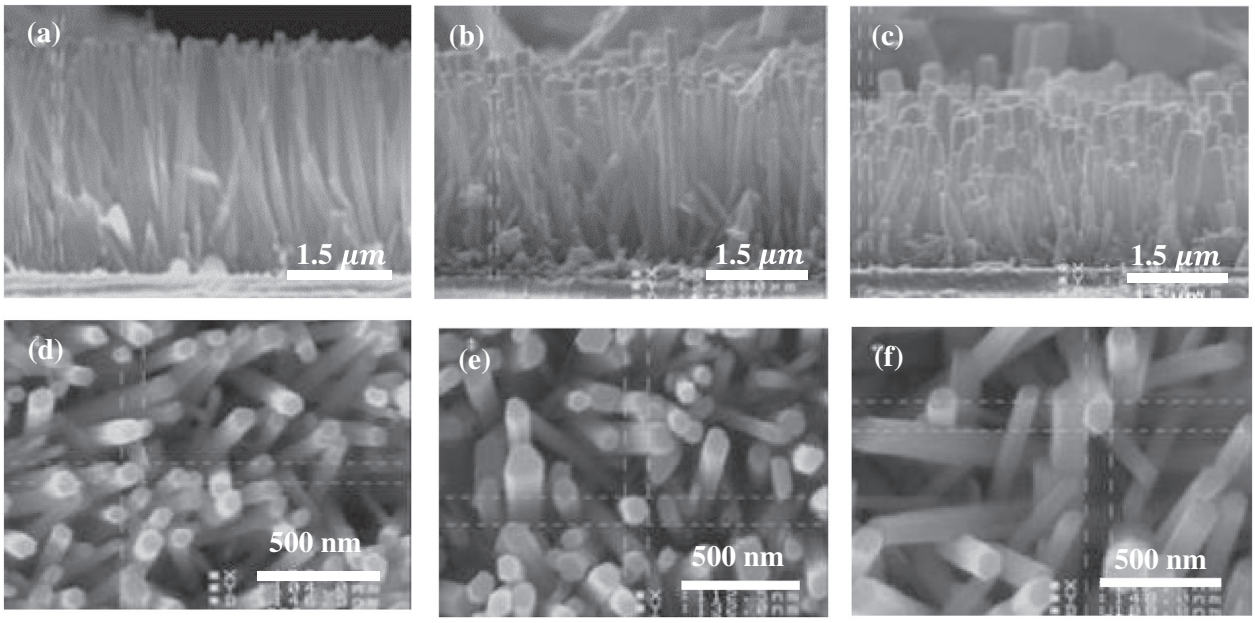

Fig. 3. FESEM cross-sectional and top-view images of ZnO nanostructures doped with (a, d) 1% Al; (b, e) 3% Al.

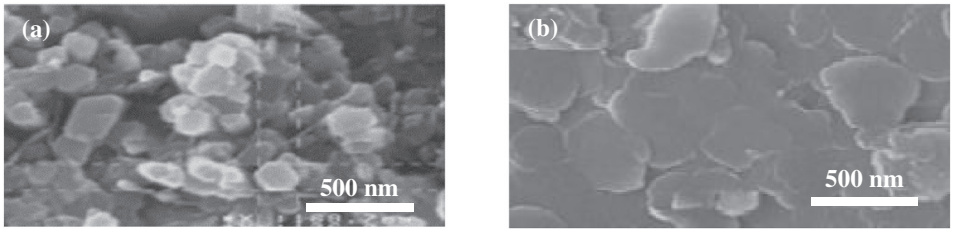

Fig. 4. FESEM images of the surface morphology of ZnO nanostructures doped with (a) 5% and (b) 7% Al.