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# Influence of annealing temperature on morphological, optical and UV detection properties of ZnO nanowires grown by chemical bath deposition

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ABSTRACT

Chemical solution deposition is a low-temperature method with possibly the lowest-cost for growing zinc oxide (ZnO) nanowires (NWs) on an amorphous glass substrate. A ZnO seed layer is needed to initialize the uniform growth of oriented nanowires. In the present work, we deposited the seed layer onto the glass substrate using radio frequency magnetron sputtering system. The ZnO NWs were fabricated on the seeded substrate by immersing them in a chemical bath containing zinc nitrate and hexamethylenetetramine (HTMA) aqueous solution. Several properties of as-grown ZnO NWs and annealed ZnO NWs at different temperatures in pure oxygen atmosphere were investigated. Well-defined ZnO nanowires almost perpendicular to substrate surface were observed through field emission scanning electron microscopy micrographs. X-ray diffraction measurements showed that all ZnO samples possessed a typical wurtzite structure with high crystallinity and no other impurity phases. The results of UV–Visible spectroscopy and room temperature photoluminescence implied that increasing the annealing temperature could have a significant influence on the performance of samples. The ZnO-based interdigitated metal–semiconductor–metal (MSM) was produced using the thermal evaporation of silver contacts. The results of current–voltage and transient response measurements demonstrate that despite using the low-cost thin film techniques, high responsivity was obtained.



## 1. Introduction

Bio-safe, multi-functional ZnO is one of the most important II–VI semiconductor materials with a wide direct band gap of 3.37 eV [1–4]. Many studies have been conducted to explore the low-cost, environmentally friendly, and highly transparent ZnO material (>80%) in the visible wavelength region [5] with large exciton energy (~60 meV) for the UV detection applications [6]. The other valuable properties of this semiconductor are high electron mobility and excellent piezoelectric behavior and the ability to be ferromagnetic. Darshana et al. have shown an additional evidence for the defect-induced ferromagnetism in undoped and transition metal doped ZnO nanocrystals [7]. Among the different morphologies of ZnO nanostructures, the one-dimensional (1D) structures are ideal systems because of their potential for direct usage in device fabrication [8,9]. The unique physical and chemical properties of 1D nanostructures, such as nanowires and nanotubes, make them as good candidates for the two or three-dimensional systems (as "thin film" or "superlattice") [10,11]. The 1D ZnO nanostructures are fabricated using various methods including thermal chemical vapor deposition (CVD) [12], metal organic chemical vapor deposition (MOCVD) [13], molecular beam epitaxy (MBE) [14], atomic layer deposition (ALD) [15], hydrothermal synthesis [16–18], successive ionic layer adsorption and reaction (SILAR) [19], and sol–gel process [20,21]. Among these techniques, chemical bath deposition (CBD) is well suited for the fabrication of ZnO nanostructures owing to its simplicity of preparation, satisfactory stability, inexpensive equipment, low deposition temperature (<100 °C), and good compatibility with flexible substrates [22–24]. To eliminate the mismatch and strain between the amorphous substrate and ZnO layer, it is necessary to prepare the thin film of zinc nucleation sites. Common pre-seeding methods are in-situ thermal decomposition of zinc acetate crystallites [25], spin coating of ZnO nanoparticles [26], and the use of physical vapor deposition methods [27,28] to deposit ZnO thin films. Pre-seeding can be performed in conjunction with top-down patterning methods such as electron beam lithography and nanosphere lithography to designate nucleation sites prior to growth [29]. The uniform deposition on substrates with large

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area and stability, better adhesion, and higher film density compared with the chemical approach, and low-temperature deposition among physical approach can be achieved by the sputtering techniques [30].

In the current study, we fabricated a low-cost MSM UV photodetector (PD) based on ZnO NW arrays prepared by CBD on the glass substrate. The influence of thermal treatment on the morphology and the optical properties of ZnO NWs and photodetector responsivity were also studied. In addition, we purposed a special thermal treatment and combination of physical and chemical methods to reach high sensitivity and detectivity.

## 2. Experimental details

### 2.1. Preparation of the ZnO seed layers

To avoid the mismatch between the glass substrate and ZnO nanowires, a textured ZnO thin film was deposited on the top of a non-epitaxial substrate (such as silicon or glass) to act as a nanowire nucleation layer [31].

In this study, magnetron sputter coating system (Salan Co., Iran) was used to deposit the nano-structured ZnO film onto the surface of the glass substrate. The RF magnetron sputtering was performed because it creates higher coverage density of the active nucleation sites. The sputtering was carried out at ambient temperature using ZnO (99.99% purity) target in the presence of argon (99.999% purity) gas at the radio frequency (RF) of 13.56 MHz, where the target-to-substrates distance was 5 cm. The rate of argon flow was maintained at 20 sccm (standard cubic centimeters per minute). The working pressure was 30 mTorr with the sputtering power of 100 W. The thickness of the prepared films was approximately 100 nm. All films were deposited at room temperature and the target was water-cooled.

### 2.2. Preparation of the ZnO NW arrays

Chemical bath deposition approach was used to fabricate the vertically aligned ZnO nanowire arrays. It is worth mentioning all chemical materials were purchased from Merk Co., Germany, and used as received without further purification. In the synthesizing process, 50 ml of aqueous solution of zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 98% purity) with the concentration of 16 mM was mixed with 50 ml aqueous solution of hexamethylenetetramine (HTMA) ($C_6H_{12}N_4$, 99%) with the concentration of 24 mM, at the temperature 70 °C. Then, the glass substrate functionalized with the ZnO seed film was kept in this solution in a beaker at the temperature of 90 °C for 3.5 h. The aqueous solutions of zinc nitrate and HMTA can produce the following chemical reactions [32]:

$$C_6H_{12}N_4 + 6H_2O \leftrightarrow 4NH_3 + 6HCHO \quad (1)$$

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \quad (2)$$

$$Zn^{2+} + 4NH_3 \leftrightarrow [Zn(NH_3)_4]^{2+} \quad (3)$$

$$Zn^{2+} + 2OH^- \leftrightarrow Zn(OH) \quad (4)$$

$$Zn(OH)_2 \leftrightarrow ZnO - NWs + H_2O \quad (5)$$

The concentration of HMTA plays an important role since $OH^-$ strongly affects the reaction that produces nanostructured [33]. When the $OH^-$ ions were supersaturated, they would combine with $Zn^{2+}$ to form intermediate products such as $Zn(OH)_2$ in the solution. Since the zinc hydroxide is easily dehydrated and the solution was maintained at the temperature of 90 °C, the intermediate products would quickly convert to ZnO NWs.

After growing the nanowires by CBD on the seeded substrates, the samples were taken out from the CBD solution and rinsed with deionized (DI) water and ethanol, and then dried under airflow. Since the grown ZnO thin films have an unstable state [34], the post-annealing leads to rich crystalline quality. Post-annealing in oxygen atmosphere improved the morphology and structural quality of the grown ZnO layer due to the removal of dangling bond [35].

The grown ZnO NWs were subjected to the thermal annealing in oxygen atmosphere under different annealing temperatures between 350 °C to 450 °C. The samples were kept in these temperatures for a period of 1 h to reach homogeneous crystalline structure. The heating rate in each annealing process to reach the final annealing temperature was maintained at 20 °C/min and the rate of oxygen flow was set at 10 sccm. Finally, all of the samples were cool down under free cooling.

### 2.3. UV photodetector fabrication

A 150 nm silver contact was deposited using a metal mask based on the pattern of the contact structure by thermal evaporation. The pressure and rate of deposition were fixed at $10^{-6}$ Torr and 1 Å/s, respectively. The structure of the MSM photodetector consists of two interdigitated contacts (electrodes) with five fingers for each electrode. Each finger has a width of 250 μm, the length of 3.5 mm with a 400 μm spacing between the fingers The schematic description of various stages in the fabrication of a ZnO NW photodetector is shown in Fig. 1.

### 2.4. Characterization

The morphology and the structure of the ZnO nanowires were characterized by scanning electron microscopy (SEM) (VEGA 3, TESCAN, Czech Republic) and X-ray diffraction (XRD) (PANalytical X'Pert Pro MPD, Netherland) using monochromatic Cu Kα radiation (λ = 1.54 Å) with a thin film accessory. The XRD data were obtained via grazing technique on the thin films. The UV–Visible absorption measurement was used for the study of optical properties. The optical characterization of the ZnO nanowire films was performed using UV–Visible absorption spectroscopy (Shimadzu Corp., 1800, Japan) and room temperature photoluminescence (PL) spectroscopy (Perkin-Elmer, LS55, USA). The current–voltage (I–V) characteristics of the device were measured using an Agilent 414HB semiconductor parameter analyzer at room temperature.

## 3. Results and discussion

### 3.1. ZnO seed layer morphology

A FESEM micrograph of the glass substrate seeded with ZnO nanowires is shown in Fig. 2(a–b). These figures show the nanowires growth in various directions, resulting in a flower-like growth pattern (Fig. 2b), because of multifarious orientations of the seed crystallites (Fig. 2a).

The XRD test was performed on seeded substrates before wire growth for ZnO seed characterization (Fig. 3). Prior to growth, the aligned seeds showed only a (002) reflection, indicating their complete c-axis texturing. The sample indicated a randomly oriented hexagonal wurtzite structure of ZnO (JCPDS card No. 01-079-0207). The wurtzite ZnO structure is most common considering its stability under ambient atmospheres [36].

Meanwhile, the intensity of the diffraction peak corresponding to the (002) orientation indicated a slight increase. The (002) diffraction peak was indexed at $2\theta = 34.2°$, where its full width at half