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Optoelectronic properties of cauliflower like ZnO–ZnO nanorod/p-Si heterostructure

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ABSTRACT

The cauliflower like ZnO nanostructures are grown on ZnO nanorods using spray pyrolysis method. First, ZnO nanorod arrays are grown on p-type silicon substrate without catalyst by chemical vapor transport and condensation method in a horizontal tube furnace. Afterwards, the cauliflower like ZnO nanostructures is deposited on top of the ZnO nanorod array. The PL spectra of cauliflower like ZnO nanostructures consist of UV emission bands around 387 nm and a visible emission at ~440 nm. The current–voltage (*I*–*V*) measurement under dark and UV illumination condition are performed to study photodetection of the cauliflower like ZnO–ZnO nanorod/p-Si heterostructure. The experimental data of dark *I*–*V* curve show that the tunneling-recombination model is the dominant current transport mechanism in our device heterostructure below 2 V. It is observed that UV photons are absorbed in ZnO and device exhibit 0.07 A/W responsivity at 5 V reverse bias which correspond to quantum efficiency of 26%.

1. Introduction

Zinc oxide (ZnO) is a direct wide band gap (3.37 eV) wurtzite semiconductor with large exciton binding energy (60 meV) at room temperature which has attracted considerable attention during last decade. Among different growth morphologies of ZnO nanostructures, ZnO nanowires (NWs) and nanorods have drown noticeable interest for application in optoelectronic devices due to high crystalline quality, large surface area, and their ability to provide a straightforward path for charge transport [1–5]. In some optoelectronic devices such as photo detectors and light emitting diodes (LEDs), for vertical integration of nanowire array, they should be electrically connected to a metallic contact. Therefore, for better electrical and mechanical stability it is necessary to fill the space between nanowires and nanorods with insulating materials like polymers [6,7]. In recent years, some groups presented formation of ZnO layer by metal organic chemical vapor deposition (MOCVD) method on top of ZnO nanowire arrays as an alternative way of connecting ZnO NWs to metal contact [8,9]. MOCVD is believed to be one of the simplest techniques have been used to grow ZnO films such as pulsed laser deposition [10,11], molecular beam epitaxy [12], and sputtering [13,14]. However, it has some drawbacks like expensive apparatus and complicated procedure in comparison to solution based methods. Spray pyrolysis is a solution based technique which is suitable for the growth of ZnO layers and nanostructures because of simplicity, low temperature process, and most importantly suitability for large scale production on arbitrary substrates. ZnO thin films prepared by spray pyrolysis method can be used as transparent electrodes in many optoelectronic devices such as solar cells [15].

In this study, a hybrid structure consists of ZnO cauliflower like film grown on ZnO nanorod array is introduced. The ZnO nanorod array is grown by chemical vapor transport and condensation method (CVTC) on silicon substrate without catalyst. The cauliflower ZnO nanostructures are deposited on ZnO nanorod arrays by spray pyrolysis method. Morphology, crystal structure, optical and electrical properties of this structure photodiode are investigated. To our Knowledge this is a first report of ZnO cauliflower like nanostructures grown on ZnO nanorod array by spray pyrolysis method.

2. Experiments

The synthesis of ZnO nanorod arrays is carried out by a catalyst free chemical vapor transport and condensation method in a horizontal quartz tube furnace on the p-type Si (100) wafers with resistivity of 1–5 Ω cm and thickness of 525 ± 20 μm. The source material is mixture of zinc oxide powder (99%, Merck) and graphite powder (99%, LOBA chemie) with equal amounts (a weight ratio of 1:1). It is placed at the central hot zone of the furnace. The furnace is heated to 1005 °C at a rate of 20 °C/min and is kept at this temperature for 1 h under constant flow of high purity Ar gas at a rate

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of 210 sccm while the Si substrate is placed downstream along the direction of gas flow which resulted the substrate temperature of ~640 ± 40 °C. After the desired growth process, the furnace is turned off to be cooled down to room temperature.

ZnO cauliflower like nanostructures is grown on ZnO nanorod array using spray pyrolysis. To prepare the 0.3 M solution, zinc acetate dehydrate ($Zn(CH_3COO)_2$, $2H_2O$) is dissolved in methanol and deionized water (3:1). Few drops of acetic acid are added to improve the clarity of the solution and to prevent formation of zinc hydroxide compounds. The starting solution is sprayed on the ZnO nanorod array using medical nebulizer (BREMED; BD 5002) during 45 min. The carrier gas is filtered compressed air. The nozzle to substrate distance is ~8 cm. During deposition process the substrate temperature is kept constant on hot plate using electronic temperature controller with accuracy of ±5 °C. After deposition the samples are allowed to cool down to room temperature.

The crystal structure of ZnO nanostructures are characterized by X-ray diffraction (XRD; Philips X' Pert) with Co Kα radiation (λ = 0.1788 nm). Surface morphology of the samples is investigated by using field emission scanning electron microscope (FESEM; Hitachi S-4166). The photoluminescence measurements are made at room temperature using a 325 nm excitation of fluorescence spectrophotometer (Cary Eclipse). The electrical measurements are performed in a two terminal configuration using Sanwa PC5000 and Dual display ESCORT 3146A multimeters. A 325 nm He–Cd laser (Melles Griot) is used as a light source for *I*–*V* measurements.

3. Results and discussions

Top view and cross section SEM analysis are used to investigate morphology of ZnO nanostructures and density of ZnO nanorod arrays. Fig. 1 shows a dense ZnO nanorod array on Si substrate using CVTC method without catalyst. The density of nanorods is estimated to be 7×10^8 wire per cm^2.

Fig. 2a and b shows top view and cross section SEM images of ZnO nanostructures grown on nanorod arrays at substrate temperatures 450 °C. From the cross section SEM images the height of cauliflower like structures deposited at 450 °C is ~1.54 μm.

From SEM images and the proposed process for growth of CuO flower like structure on ZnO nanowire arrays by Jung et al. [16], a suggested formation process for ZnO flower like structures is as follow: in the initial stage of growth, ZnO particles are randomly deposited on the tip of ZnO rods and act as nuclei. Then, these nuclei grow by aggregation of ZnO particles and form disks and plates. The results show that the density of rod arrays is an effective parameter on surface morphology of structures. Fig. 3 shows top view SEM images of flower like structures grow on tip of low density ZnO rod array under different magnifications. The higher magnification SEM images (Fig. 3b) show that the flower like structures formed from ZnO plates. Each plate is assembled from small ZnO nanoparticles and it has triangular shape tip. The XRD pattern of this structure reveals that (1 0 0) is the preferential growth direction of flower like structures grow on tip of low density ZnO rods.

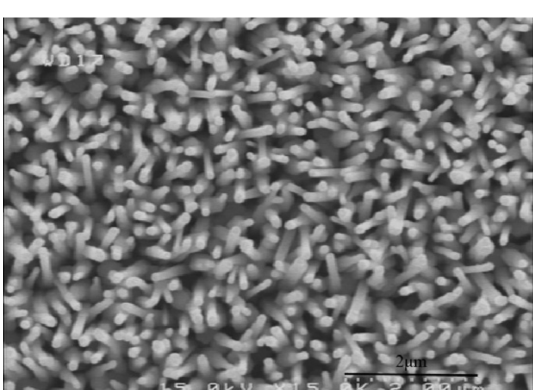

Fig. 1. Top view FE SEM image of ZnO nanorod array grown on Si substrate. The scale bar is 2 μm.

Crystal structure of nanostructures deposited at 450 °C was investigated by the X-ray diffraction analysis in the 30–80° range of 2θ. As shown in Fig. 4, the diffraction pattern indicates polycrystalline hexagonal-wurtzite structure with lattice constants of *a* = 3.2511 Å and *c* = 5.2078 that are in good agreement with the standard data i.e. *a* = 3.2498 Å and *c* = 5.2066 Å (JCPDS card 36-1451). All the peaks in the spectra can be indexed to the crystal structure of ZnO. The higher intensity of (0 0 2) peak indicates the preferred orientation along their *c*-axis.

The room temperature photoluminescence spectra of nanorods and cauliflower film are compared in Fig. 5. The PL spectra consist of a near band edge UV emission and a visible emission band. The UV emission band of nanorods and cauliflower nanostructures are centered at ~383 nm and ~387 nm, respectively. The band gap is evaluated to be ~3.30 eV for nanorods and ~3.26 eV for cauliflower nanostructures grown on rods. The band gap narrowing can be related to the localization energy of surface states which reduce the emitted photon energy in PL spectrum [17]. The surface states can act as non irradiative recombination centers which is attributed to lowering the PL intensity of UV emission peak of cauliflower like nanostructures compared to ZnO nanorods (Fig. 5). The origin of visible emission bands observed in PL spectra has not been conclusively established and is related to deep level defect emission [18]. The broad visible emission band in the PL spectrum of ZnO nanorods centered at ~496 nm is related to oxygen vacancies [19] while the visible emission of cauliflower nanostructures centered at ~440 nm. Comparing PL spectra show that a shoulder located at around 440 nm in PL spectra of nanorods before spray, transforms to peak in the PL of cauliflower like nanostructures grown by spray pyrolysis. This difference between the PL spectra is observed in other samples fabricated by this method. The proposed hypothesis related visible emission band around 446 nm to shallow donor-oxygen vacancy transition and Zn interstitials [20,21].

I–*V* characteristics of the hybrid structure are measured in dark and under UV illumination by changing bias voltage from +5 to −5 V. A 325 nm He–Cd laser with optical power density of 4 mW is used as an UV excitation source. The *I*–*V* characteristics is measured by two terminals method at room temperature with 3 mm-diameter circular Ag electrodes on ZnO and backside of Si substrate as schematically illustrated in Fig. 6a.

The semi log plot of dark *I*–*V* curve under forward bias (Fig. 6b) shows two regions. For $V < 2$ V, the current increases exponentially following the equation $I \sim \exp(\alpha V)$ which is usually observed in the wide band gap p–n junction diodes due to tunneling-recombination model [22–25]. The constant α is evaluated to be ~0.65 V^{-1} by fitting the experimental data. This value falls in the range of 0.45–1.50 V^{-1} for the semiconductor junctions [26]. For $V > 2$ V, the dark *I*–*V* curve follows a power law relation of $I \sim V^2$ which is suggesting space- charge- limited current conduction [23].

Fig. 7 shows the absorption of UV light in the depletion region of ZnO. Therefore, under forward bias the current increases significantly. The photocurrent is given by,

$$I_{ph} = I_{\text{illuminated}} - I_d \tag{1}$$

where $I_{\text{illuminated}}$ is the measured current under illumination and I_d is the dark current. The photocurrent is almost 8 times higher than the dark current at 0.1 V. The significant increase of photocurrent under forward bias and 325 nm illumination is due to transmission of photogenerated electrons in ZnO nanostructures through ZnO