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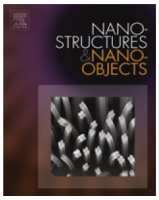

Phosphorous doping in vertically aligned ZnO nanorods grown by wet-chemical method

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HIGHLIGHTS

- Synthesis of ZnO nanorods perpendicular to the glass substrate surface via two step method comprises of sputtering and chemical growth.
- Phosphorous (P) doping through vacuum evaporation of P on ZnO nanorods and then rapid thermal annealing (RTA) in vacuum.
- Microstructural study through SEM and XRD to confirm the growth of well-aligned hexagonal ZnO with Zn-site being substituted by P ions.
- Study of vibrational properties (FTIR and Raman) and Optical properties (UV–VIS–NIR and Photoluminescence) also confirmed P doping in ZnO.

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ABSTRACT

The synthesis of well-aligned highly crystalline phosphorous (P) doped ZnO nanorods (ZnO:P) on glass substrates is demonstrated here. Vertically aligned ZnO nanorods are fabricated by a two-step method comprises of nanocrystalline ZnO seed layer formation by dc sputtering technique followed by solution growth of ZnO nanorods. To incorporate P, aligned ZnO nanorod films are exposed to P vapor in a vacuum chamber and then subjected to rapid thermal annealing in vacuum at an elevated temperature of 450 °C. Scanning electron microscopy and X-ray diffraction measurement confirm the growth of highly crystalline well aligned hexagonal ZnO nanorods that are perpendicular to the substrate surface. The optical band gap estimated from the transmittance spectra recorded by a UV–VIS–NIR spectrophotometer is 0.24 eV lower for ZnO:P compared to ZnO nanorods. Vibrational properties of ZnO:P nanorods are studied by FTIR and Raman spectra. Raman peak appeared at 355 cm^{-1} for ZnO:P is due to the Zn-site substituted by phosphorous. For ZnO nanorods, the room temperature photoluminescence (PL) spectra shows a sharp UV emission peak due to near band edge transition and a broad blue–green emission peak due to defect related transition. The observed red shift for the UV emission peak in the ZnO:P nanorods is associated with the shrinking band gap whereas the intense and broad blue–green emission peak is due to defects introduced with P doping.

1. Introduction

One dimensional zinc oxide (ZnO) nanostructures are most promising materials for optoelectronic devices like light emitting diodes, UV photo detectors and solar cell [1,2]. ZnO being a wide band gap (3.37 eV at RT) compound semiconductor with large excitonic binding energy (60 meV), can be fabricated in various nano-structural form which are suitable for advanced nanodevices [3–5]. In addition to above properties, the availability of single crystal substrates and relatively low growth temperatures have made ZnO more desirable than GaN for optoelectronic applications [6]. But the biggest challenge which remains till date, is the fabrication of ZnO based p–n homojunction because as-grown ZnO even in the presence of various dopants normally shows n-type conductivity due to presence of native defects like oxygen vacancy (V_o), zinc interstitials (Zn_i) and/or H incorporation [6–8].

Recently, there is an increasing demand of developing reliable, efficient and reproducible p-type ZnO for ZnO-based optoelectronic and spintronic applications. For this purpose, various dopants of group V elements, such as, nitrogen (N) [9–11], phosphorous (P) [12–15], arsenic (As) [16–18] and antimony (Sb) [19–21] have been adopted to synthesize p-type ZnO structures. Considering the mismatch in ionic radii for N (1.68), P (2.12 Å), As (2.22 Å), and Sb (2.45 Å) as compared to O (1.38 Å), N and P

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solubility in ZnO must be highest among these elements [22]. However, N incorporation at the O-site as molecular form neutralizes the p-type nature of ZnO [23]. Therefore the next best choice is P doping for producing p-type ZnO. P doped ZnO films have demonstrated high carrier concentration, low resistivity as well as good mobility [12,14]. Besides, a co-doping technique for p-type ZnO synthesis is also reported by some researchers, where N together with group III elements, like, Al, Ga are doped into ZnO [24,25]. Very recently Mannama et al. reported P and N co-doping in ZnO films with P substituted at Zn site and N at O site [23]. It has been widely [16] proposed that the origin of p-type conduction in the ZnO is due to the formation of defect complex and shallow acceptor levels [23,26].

There are several difficulties with p-type phosphorus doped ZnO nano-structures, like, low crystalline quality, uncontrolled dopant concentration, and use of toxic chemicals (Zn_3P_2) for synthesis etc. [27,28]. Furthermore, the phosphorus doping mechanism into ZnO nanostructures is still not well understood, which is believed to be the main drawback for synthesis of reproducible and efficient phosphorus-doped p-type ZnO in practice. There are various methods that have been adopted for p-type doping (P, Sb) in ZnO, such as, Molecular beam epitaxy [20], pulse laser deposition (PLD) [22,23,29], chemical vapor deposition [30], radio-frequency magnetron sputtering [31] etc. The commonly used precursors for P doping in ZnO are P_2O_5 and Zn_3P_2. PLD is the most popular technique for P doping in ZnO but the film often suffer from the difficulties as mentioned above. In most of the P-doping methods, dopants are incorporated in the host matrix using dopant precursor at the time of ZnO growth that may lead in poor crystalline quality of ZnO. We propose a method comprises of post treatment on well aligned highly crystalline ZnO nanorods for P incorporation in ZnO that maintains the quality of the host ZnO nanorods.

Here we report a simple way of P doping into vertically aligned ZnO nanorods through hybrid wet chemical deposition of nanorods followed by phosphorous evaporation and rapid thermal annealing while persisting the crystalline quality. The P doped ZnO nanorods are characterized by scanning electron microscope (SEM), X-ray diffractometer (XRD), Optical spectroscope, Fourier Transform Infra-Red spectroscope (FTIR), Raman and Photoluminescence (PL) measurements. The chemical composition of the ZnO nanorods and the quantity of doped P into ZnO nanorods are estimated by energy dispersive X-ray diffraction (EDX) analysis. The quality of the films and effect of P doping has been evaluated in details in comparison to undoped vertically aligned ZnO nanorods.

2. Experimental details

Well aligned ZnO nanorods which are vertical to the glass substrates were deposited by the technique described in Ref. [32]. This method is comprised of both physical vapor deposition technique and chemical deposition method. A very thin layer (thickness ~70 nm) of nanocrystalline ZnO was deposited on glass substrate by high pressure dc sputtering technique at room temperature. A highly pure ZnO target was sputtered for 30 min at argon gas pressure of 30 mbar maintaining the applied negative voltage of 1 kV at the target holder with reference to the substrate holder. These nanocrystalline ZnO layer act as the seed layer during the solution growth of ZnO nanorods. The substrate having ZnO seed layer was placed vertically into the aqueous solution of zinc nitrate hexahydrate (0.01M) and sodium hydroxide (0.4M) which was mixed homogeneously using a magnetic stirrer. During the whole growth period of 45 min the temperature of the solution was kept constant at 70 °C. The pH of the solution was maintained at ~11. After taking out of the solution bath the film surface was washed properly with deionized water and then dried in an air oven at 120 °C. The seed layer containing ZnO nanocrystallites play the key role for vertical alignment of the ZnO nanorods as they act as the nucleation center for the nanorod growth. The size and number density of nanocrystallites defines the diameter and number density of the nanorods [32,33]. The films are very sticky to the substrate and also the quality of the nanorods are excellent as the sputtered ZnO seed layer produces very small interface strain and less no of surface defects. In the solution, the growth of ZnO along the c-axis is very fast compared to others as the ZnO is a polar molecule having the direction of polarization along the c-axis. The well crystalline c-axis oriented ZnO nanocrystallites act as the nucleation centers and monitor the alignment of ZnO nanorods. This relatively easy, cost-effective and environment friendly method of producing ZnO nanorod arrays has immense implications for both fundamental studies and technological development.

ZnO nanorods that are vertically aligned to the glass substrate, was exposed to phosphorous (P) vapor produced in a high vacuum chamber that was initially evacuated to a base pressure of $\sim 10^{-6}$ Torr. The alumina crucible loaded with Red P (99.99% pure) was heated indirectly by heavy duty tungsten bucket heater to evaporate P inside the vacuum chamber. The top of the alumina crucible was covered with porous zinc wool to control the evaporation rate that leads in maintaining the uniform P vapor pressure in the chamber as P tends to ooze out with temperature increase for its non-uniform evaporation rate. The ZnO nanorod sample was kept under constant P vapor pressure of $\sim 10^{-5}$ Torr for 5 min. Then the ZnO nanorods film having a thin surficial layer of P (thickness ~10 nm) was subjected to rapid thermal annealing (RTA) in vacuum. The temperature was rapidly increased to 400 °C and then cooled down to room temperature after 2 min.

The surface morphology of the ZnO:P nanorod thin film was recorded by a Quanta FEG 250 scanning electron microscope (SEM) operated at 25 kV. The EDX spectra was recorded with the setup attached to the SEM. A PANalytical X-PERT PRO X-ray diffractometer (XRD) using Cu K_α radiation (0.154 nm) was used to obtain the micro-structural information. Optical studies were performed by measuring the transmittance in wavelength region of $\lambda = 300$–1100 nm at room temperature using a spectrophotometer (Hitachi-U3410). The spectra were recorded with a resolution of $\lambda \sim 0.07$ nm along with a photometric accuracy of ±0.3% for transmittance measurements. Raman spectra were recorded using Renishaw inVia micro-Raman spectrometer using 514 nm Argon laser. Fourier Transform Infra-Red spectra were recorded in the range of 400–4000 cm^{-1} by using a PerkinElmer FTIR spectrometer. Photoluminescence (PL; Fluorolog, Jobin-Yvon, Horiba) measurements were recorded at 300 K using excitation of 258 nm radiation for detecting PL peaks in 300–700 nm range.

3. Results and discussion

Fig. 1 shows the SEM image of P incorporated ZnO nanorods (ZnO:P) which are mostly aligned perpendicular to the substrate surface. Fig. 1(a) shows the top surface of ZnO:P nanorod film through a tilted view while the side view of ZnO:P nanorods on the glass substrate is presented in Fig. 1(b). The inset of Fig. 1(a) shows the SEM image of undoped ZnO nanorods on glass substrate. The morphology of the ZnO nanorod thin films remain unchanged upon P incorporation in it. The dense array of nanorods have average diameter of 100 nm and average length of 1 μm which are calculated from these tilted top view and side view of the SEM images. These SEM images imply that nanorods are uniformly grown on the nanometer sized seed layer of ZnO and are vertically oriented on the glass substrate. The EDX spectra of undoped ZnO nanorods and ZnO:P nanorods are shown in Fig. 2(a) and (b) respectively which confirms the presence of P in the film (Fig. 2(b)). The P doping amount is 2.98% (atomic) along with Zn and O. The

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