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The growth and the ultraviolet photoresponse properties of the horizontal growth ZnO nanorods

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ABSTRACT

The horizontal ZnO nanorods (NRs) were grown by using a low temperature hydrothermal method between the lithographic ZnO interdigital electrodes. In order to horizontally grow the ZnO nanorods, the vertical growth was restrained by coating with the photoresist on the surface nucleation sites. By controlling the distance between the electrodes, only the electrodes for an interval of 7 µm can be connected by the horizontal nanorods to form device. The electrical property of the device was measured. The detector showed a narrow ultraviolet photoresponse with a response peak at 379 nm, which was according with the peak of the photoluminescence. The mechanism of photoresponse was discussed.

1. Introduction

Recently, the design and the fabrication of nanomaterials and nanodevices have become one of the most active research fields due to their unique properties and potential applications [1–3]. Among the various nanomaterials, zinc oxide (ZnO) is a remarkable one owing to its special properties, such as the wide band gap of 3.37 eV, high exciton binding energy and its high thermal and mechanical stabilities [4]. The various-shaped ZnO nanostructures, including nanobelts, nanowires and nanorings [5,6] have been studied for ultraviolet (UV) optoelectronic application. Various nanodevices based on one dimensional (1D) ZnO nanostructures have exhibited special properties, such as laser diodes [7], light emitting diodes (LED) [8,9], ultraviolet detector [10–12], gas sensors [13,14] etc..

However, the fabrication of the ZnO NRs devices is still a challenge. There are two main methods to make nanodevices using 1D nanostructure. One is to use a single nanowire to build nanodevices, in which some special equipment is needed to operate in nanoscale [15,16]. The other one is to design nanodevices based on nanowires array with some traditional methods [12,17]. The essentials for the second method are the controllable growth of nanowires and the proper design of the nanodevices. The vertical aligned ZnO nanowires array is often used as a building block to fabricate optoelectronic devices [18]. In this study, we tried to grow horizontal ZnO nanorods between the patterned electrodes. The horizontal nanorods could directly fabricated nanodevices on electrodes. Our method can also avoid the insulation filling and surface etching processes in making the vertically grown ZnO nanorods based devices. Furthermore, we also characterized the ultraviolet photoresponse properties of the horizontal nanorods.

2. Experimental

The growth processes of the horizontal ZnO nanorods are listed as follows. First a ZnO thin film with the thickness of 400 nm was grown on sapphire substrate by using a sputtering method. Then a BP212-37 positive photoresist was spin-coated on the ZnO films. After the exposal and removing steps, the uncovered ZnO thin film was etched by the diluted HCl (0.001 mol/L) to form the ZnO interdigital electrodes. The ZnO nanorods were grown via a hydrothermal method. In this step, the solution contained 0.01 mol/L $Zn(CH_3COO)_2 \cdot 2H_2O$ and 0.01 mol/L hexamethylenetetramine (HMTA) which were dissolved in deionized water served as the source material [19]. The reaction was maintained at 90 °C for 12 h in a Teflon-lined stainless autoclave. After the growth the photoresist was removed by acetone.

The morphologies of the products were observed by field emission scanning electron microscopy (FESEM, Hitachi S-4800) and high resolution transmission electron microscopy (HRTEM). Photoluminescence (PL) spectra were measured by using the 325 nm line of a He–Cd laser as an excitation source. For the characterization of the UV detectors, a 150 W Xe lamp was used as the excitation source. The spectrum response was measured by a lock-in amplifier. The dark current was measured by the Hall measurement system.

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3. Results and discussions

The surface morphologies of the ZnO are shown in the SEM images (Fig. 1(a) and (b)). The fingers of ZnO interdigital electrodes are 500 μm in length and 7 μm in width. The distance between the electrodes was varied from 7 μm to 14 μm. From the magnified SEM image shown in Fig. 1(b) each electrode edge is not so sharp. Fig. 1(c) and (d) show the SEM images of ZnO nanorods grown on the interdigital electrodes when the photoresist on the ZnO film surface was removed before the hydrothermal growth process. The ZnO NWs are grown to be almost perpendicular to the film surface with a diameter less than 100 nm. The ZnO nanorods on each electrode could not be connected with the ones on the adjacent electrode.

To grow ZnO nanorods on the side face of the interdigital electrodes, the photoresist should be removed after the hydrothermal growth step. The surface morphologies of ZnO nanorods grown following this growth process are shown in Fig. 2. The ZnO nanorods could be observed grown almost horizontally on the substrate surface. The interelectrode spacing was adjusted at 7 μm, 10 μm and 14 μm respectively. Fig. 2(a) and (b) shows that the lengths of horizontal nanorods are around 5 μm and lots of nanorods from the adjacent electrodes could connect with each other for the interval of 7 μm. The inset image of Fig. 2(b) shows the HRTEM of the cross section for the two connected ZnO nanorods. Because of the difference of the focalization, we could just observe one nanorod detailed at one time. From the HRTEM image, the lattice planes could be clearly observed with the lattice spacing of 0.26 nm, which means each of the connected ZnO nanorods keeps the single crystalline structure. For the interelectrode spacing of 10 μm, only a few long nanorods tips could touch each other (Fig. 2(c)). With the spacing increasing to 14 μm, the tips of nanorods are apart with the spacing of 2 μm (Fig. 2(d)).

Fig. 3 shows the electronic and optical properties of the ZnO horizontal nanorods. The electronic measurement also proved the connection for the sample with the interelectrode spacing of 7 μm. To fabricate a simple ZnO nanorods device, we put indium on the two interdigital electrodes. Fig. 3(a) inset image is the I–V curve of this device, from which a linear relationship is observed with the resistance of 8 MΩ. This result indicates that the Ohm contacts are formed by the interfaces of In and ZnO film, ZnO film and ZnO NRs. However, for the samples with interelectrode spacing of 10 μm and 14 μm, no current could be detected. Fig. 3(a) shows the photoresponse characteristic of the ZnO nanorods UV detector under a bias voltage of 5 V. The photoresponse curve shows only a narrow UV detection band centered at 379 nm with a maximum responsivity of 12.1 mA/W.

The dash line in Fig. 3(b) stands for the PL spectra of the vertically ZnO NWs. The peak of the PL spectrum is at 378 nm. As a comparison, the PL spectra of the horizontal ZnO NRs (the solid line) is given in Fig. 3(b), in which a UV emission located at 381 nm could be observed. The little red shift is caused by increasing the diameter of the ZnO NRs. This photoresponse is quite different to other ZnO based UV detectors, which shows a quite narrow photoresponse peak in the UV region. The cutoff wavelength is located at 390 nm. For the photons with high energy (higher than 3.26 eV) the photoresponse decreases rapidly. The narrow photoresponse peak is assumed from the effect of the surface defects [13,20]. Due to the large surface-to-volume ratio the transport and photoconduction properties of 1D nanostructure could be affected by the trapping at surface states. Different groups have shown that the adsorption and desorption of oxygen molecules governed the photoconduction for ZnO nanostructures. Under the illumination with the photon energy above the band gap of ZnO, electron-hole pairs are photogenerated. Then, the holes migrate to the surface and discharge the negatively charged adsorption oxygen ions. The separated electrons are either collected at the anode or recombined with holes. This process is strongly depending on the surface defects state in the ZnO nanostructures. Especially, when the photon energy increases, the penetration depth decreases and high energy photons thus become more surface sensitive. That is, the photogenerated electrons have more probabilities to recombine with the holes if the holes do not migrate to the surface quickly, which could result in the decreasing of photoresponse. To further understand the defects properties in ZnO nanorods, the low temperature PL measurement was performed at 90 K by using a micro-PL system. As shown in Fig. 3(b) inset, a dominated PL emission peak located at 3.317 eV could be observed with the concomitance of a weak emission centered at 3.238 eV. The origination of the emission at 3.317 eV is attributed to the radiative recombination of donor–acceptor-pairs (DAP) [21,22]. And the peak around 3.238 eV is ascribed to the

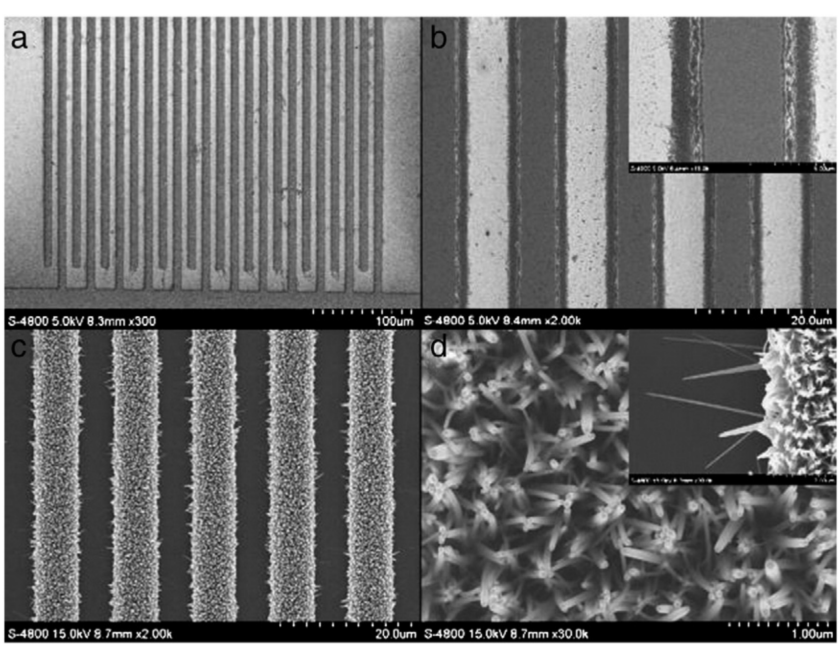

Fig. 1. (a) and (b) SEM images of the ZnO interdigital electrodes, (c) and (d) SEM images of the ZnO nanorods grown on the interdigital electrodes.

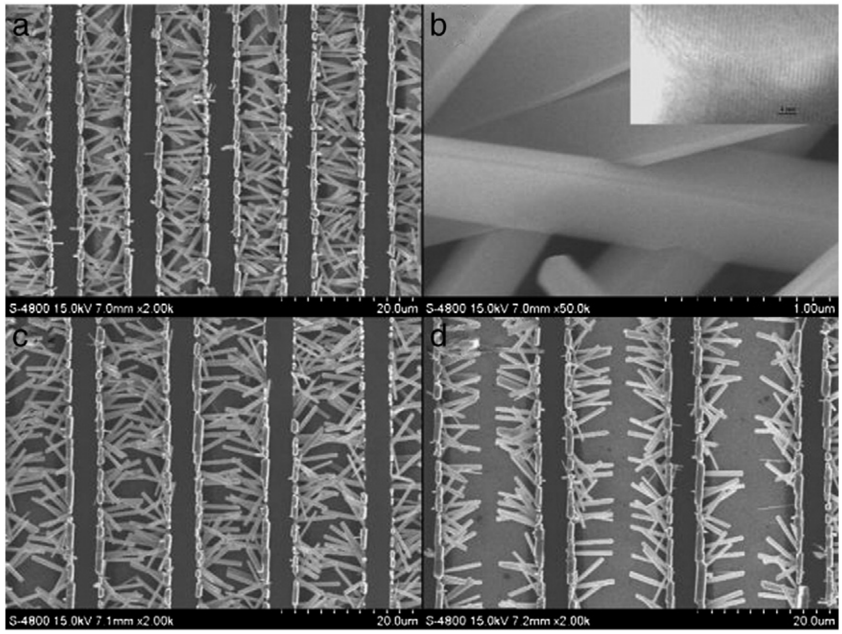

Fig. 2. The SEM images of growing the horizontal ZnO NRs at different interelectrode spacing. (a) 7 μm, (b) the connected section image of 7 μm, the inset image shows the HRTEM of the connected section (c) 10 μm, (d) 14 μm.

phonon replica of DAP with a phonon energy of about 70 meV. Because the as-grown ZnO nanorods are undoped ones, the zinc-vacancy (V_{Zn}) is assumed to be the origination of the hole generation, which exists in the depletion layer close to the surface [23]. Due to the presence of V_{Zn} the migration rate of the photogenerated holes can be limited, which leads to the probability of the recombination of electrons and holes. Therefore, the photoresponse of the device decreases in the short wavelength region.

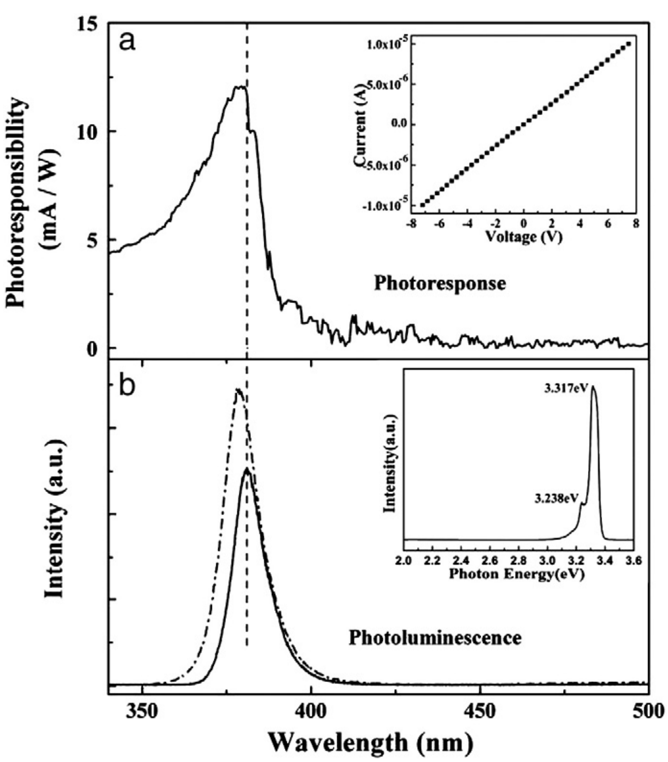

Fig. 3. (a) The photoresponse of the horizontal ZnO NRs detector, the inset image shows the IV graph (b) PL spectra of the horizontal ZnO NRs (the solid line) and vertically ZnO NWs (the dash line). The inset image shows the low temperature PL spectra of horizontal ZnO NRs.

4. Conclusion

In conclusion, by controlling the growth steps the ZnO nanorods could be grown horizontally on the side surface of the ZnO interdigital electrode with the hydrothermal method. The diameters of the as grown ZnO nanorods were around 300 nm with lengths of 5 μm. The nanorods could connect with each other with the interelectrode spacing of 7 μm to make the electrons passing through the different electrodes. The device showed a narrow visible-blind photoresponse in the UV region. The narrow response could be attributed to the surface defects in ZnO nanorods. It was proposed that by improving the conductivity of the ZnO film and the surface properties of ZnO nanorods the photoresponse of the device could be further enhanced.

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