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Responsivity to solar irradiation and the response time of photodetectors that use ZnO nanoparticles with and without thermal annealing in pure oxygen ambient

Yow-Jon Lin[a,*], Gi-Min Chang[a], Hsing-Cheng Chang[b], Ya-Hui Chen[c]

[a] Institute of Photonics, National Changhua University of Education, Changhua 500, Taiwan
[b] Department of Automatic Control Engineering, Feng Chia University, Taichung 407, Taiwan
[c] Precision Instrument Support Center, Feng Chia University, Taichung 407, Taiwan

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ABSTRACT

The optoelectronic properties of photodetectors that use ZnO nanoparticles under illumination by sunlight are determined. To investigate the role of the oxygen-vacancy (V_O) concentration in ZnO nanoparticles on the responsivity to solar irradiation and its influence on the response time of devices that use ZnO nanoparticles, ZnO nanoparticles were annealed at 800 °C in pure oxygen ambient for 30 min. Thermal annealing leads to the improvement of the ZnO stoichiometry, increasing the crystallite size. A direct link between the responsivity to solar irradiation, the response time and the V_O concentration is established. The experimental results show the important of controlling the V_O concentration to optimize the solar-irradiation detectors that use ZnO nanoparticles.

1. Introduction

Zinc oxide (ZnO) has been extensively studied for its application to the fabrication of ultraviolet photodetectors [1–6], due to its large direct bandgap (3.3 eV). However, few reports on the responsivity to solar irradiation for ZnO-based devices can be found [7–9]. Various types of ZnO nanostructures have been synthesized and applied in electrical and optoelectronic devices [1,2,10–17]. The structure of zero-dimensional nanoparticles gives better light absorption efficiency than other dimensional structures [1,18]. The performance of optoelectronic devices is dependent on the capability of control of the optical properties of ZnO. The ZnO usually exhibits n-type semiconducting properties due to the existence of oxygen vacancies (V_O) that are regarded as donor states [19,20]. In this study, the effect of thermal annealing in pure oxygen ambient on the optical and optoelectronic properties of ZnO nanoparticles is studied for understanding the role of the V_O concentration on the sensitivity to solar irradiation and its influence on the response time.

2. Experimental

ZnO nanoparticles were prepared by the sol-gel method. The growth process is shown in Refs. [7–10,21]. The thickness of ZnO nanoparticles that was deposited on sapphire substrates is about 700 nm. Some of the as-grown ZnO samples were placed in a furnace and annealed at 800 °C in pure oxygen ambient for 30 min (referred to as oxygen-annealed ZnO samples) [22].

* Corresponding author.
E-mail address: rzr2390@yahoo.com.tw (Y.-J. Lin).

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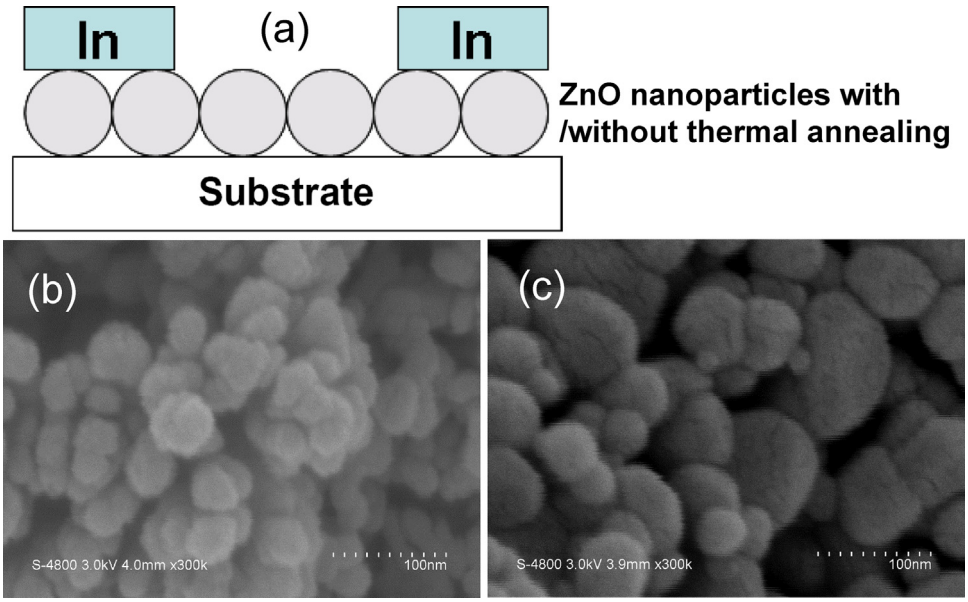

Fig. 1. (a) The structure of an In/ZnO nanoparticles/In device and the FESEM images of the (b) as-grown and (c) oxygen-annealed ZnO nanoparticles. The scale bar is 100 nm.

The grain morphologies of the nanoparticles were studied using field-emission scanning electron microscopy (FESEM). The structural properties were determined by X-ray diffraction (XRD), using Cu Kα radiation. Using a Ne–Cu laser (the 248.6 nm line) as an excitation source, the photoluminescence (PL) band was observed for ZnO nanoparticles at room temperature. In order to determine the optoelectronic properties of the as-grown and oxygen-annealed ZnO samples, the electrodes were fabricated by depositing indium metal on ZnO nanoparticles through a shadow mask. The device structure is shown in Fig. 1(a). The current–voltage (I–V) and current–time (I–t) curves were measured at room temperature using a Keithley Model-4200 semiconductor characterization system. The photo-response for the device was measured at an illumination intensity of 100 mW/cm^2, using a 150 W solar simulator with an AM 1.5G filter. The photo-response was measured by recording the current versus time and the simulated sunlight was turned on and off using a shutter.

3. Results and discussion

The FESEM images shown in Fig. 1(b) and (c) indicates the formation of ZnO nanoparticles. It is found that thermal annealing in pure oxygen ambient leads to an increase in the grain sizes of ZnO. To confirm the presence of defects in the ZnO nanoparticles and to verify the effects of these defects, the PL spectra for the as-grown and oxygen-annealed ZnO samples were obtained. Fig. 2 shows the PL spectra for the as-grown and oxygen-annealed ZnO nanoparticles. The peak at 2.5 eV is attributed to the V_O-related emission [i.e., green luminescence (GL)] and the peak at 3.3 eV is the band-edge luminescence [19,20,23,24]. The presence of the V_O-related emission increases the visible-emission absorptivity of ZnO nanoparticles, which is useful for solar irradiation detector applications. Four types of point defects are present in pure ZnO, which generate four trap levels inside the energy gap. The vacancies in zinc and oxygen (that is, V_{Zn} and V_O) are treated as acceptor and donor states, but the interstitial oxygen and zinc atoms (that is, O_i and Zn_i) are acceptor and donor states, respectively [20]. The V_{Zn}-, O_i- and Zn_i-related emissions are absent in Fig. 2. Thus, V_{Zn}, O_i and Zn_i are not taken into account for the visible-emission absorptivity of ZnO nanoparticles at room temperature. Clearly, thermal annealing in pure oxygen ambient leads to a reduction in the intensity of GL, indicating the reduced number of V_O in the oxygen-annealed ZnO nanoparticles.

Fig. 2 also shows the XRD patterns for the as-grown and oxygen-annealed ZnO samples. Three peaks that respectively correspond to the (002), (100) and (101) planes, are observed for ZnO nanoparticles. All XRD peaks along the different orientations show that the structure of the nanoparticles is hexagonal wurtzite [25]. The locations of the diffraction peaks shift towards lower diffraction angles as thermal annealing in pure oxygen ambient. The reduction in the 2θ value of the diffraction peak is attributed to the combined effect of the increased c-axis length (i.e., the increased crystallite size) and the reduced number of V_O [26]. This is consistent with the PL and FESEM results.

Fig. 3(a) and (b) shows the I–V curves of In/as-grown ZnO nanoparticles/In and In/oxygen-annealed ZnO nanoparticles/In devices in the dark and under illumination by sunlight, respectively. Fig. 3(c) and (d) shows the log (|I|)–V curves of In/as-grown ZnO nanoparticles/In and In/oxygen-annealed ZnO nanoparticles/In devices in the dark and under illumination by sunlight, respectively. It is found that the value of the dark current (I_D) of In/oxygen-annealed ZnO nanoparticles/In devices is significantly smaller than that of In/as-grown ZnO nanoparticles/In devices and the value of photocurrent (I_P)