Current Applied Physics 9 (2009) 573-576

Contents lists available at ScienceDirect

Current Applied Physics

journal homepage: www.elsevier.com/locate/cap



Spatial distribution of defect in ZnO nanodisks

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ARTICLE INFO

Article history: Received 27 December 2007 Received in revised form 29 April 2008 Accepted 9 May 2008 Available online 24 May 2008

PACS: 78.55.-m 78.30.-j 81.07.-b

Keywords: Raman mapping Photoluminescence mapping Defect distribution

ABSTRACT

ZnO nanodisks were fabricated by vapor-vapor transport using zinc powder as source material. The photoluminescence (PL) and Raman scattering spectra were investigated. Based on the mapping technology, the Raman signals combined with PL were used to construct images, which revealed the spatial distribution of defect in ZnO nanodisks. It provides an intuitive method to understand the defect distribution and further helpful to growth control of crystal and design of functional materials and devices.

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1. Introduction

In recent years, zinc oxide (ZnO) has attracted considerable interests because of its wide direct bandgap, strong exciton binding energy, and potential applications in electronic and optoelectronics. Now ones have to face a critical challenge to obtain p-type ZnO in order to develop ZnO-based functional devices, such as light-emitting diode and laser diode. So far, various approaches have been proposed for p-type doping and certain progresses have been made [1–3]. Even so, how to obtain stable and reliable p-type ZnO is still a problem. It is very important to understand the generation and distribution of defects in ZnO crystal for effective doping.

On the other hand, many investigations have revealed various nanostructures and their functions, such as nanoring [4], superlatticed nanohelix [5], nanorod-based laser [6] and generator [7]. In our previous works, a series of six symmetric ZnO nanostructures, such as nanodisk [8], twin-disk [9] and hexagram [10], were reported. Each piece of the hexagonal nanostructure is a single crystal and it is promised as a natural cavity for whisper gallery mode laser [11]. In this letter, a mapping technique was applied to investigate the spatial distribution of defects in ZnO hexagonal nanodisk

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based on photoluminescence (PL) and Raman scattering measurements. It is helpful to understand the defect behaviors and further to explore an effective p-type doping method.

2. Experiment

The ZnO nanodisks were fabricated by vapor-phase transport in two approaches. The first one (sample A) is the same with our previous report in reference [8]. The source materials of the mixture of high purity ZnO and graphite powders were placed at the end of a slender one-end sealed quartz tube. The source temperature was kept at 1000 °C and the Si substrate temperature at about 600 °C for 30-min growth. In the second method, the Zn powders in a small quartz boat were employed as source materials and placed into a slender two-end-opened quartz tube and the substrate was put in the down stream. When the source region was heated to 750 °C, the carrier gas N₂ and reaction gas O₂ were introduced with a flux ratio of 200–10 sccm. The tube furnace was kept at 1 kPa and the substrate temperature was at about 450 °C in whole process. A layer of grey product (sample B) was obtained after growth for 30 min.

The morphology of the product were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), and the microstructure were explored by X-ray diffraction (XRD) and selected area electron diffraction (SAED) in TEM system,



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respectively. Excited by a He–Cd laser at 325 nm wavelength, photoluminescence (PL) of the samples were measured through a photometer. In WITec confocal Raman microscope (CRM200), a double-frequency Nd:YAG laser at 532 nm was employed as an excitation source for the measurements of the Raman spectra. The Raman images were obtained by scanning the sample on piezo-stage, and the Raman signals were detected by a CCD through an objective lens (Olympus 100X NA 0.95) in the backscattering configuration.

3. Results and discussion

The product of sample A and sample B has the similar shape although they grew at higher temperature with ZnO as source and at lower temperature with Zn as source, respectively. Fig. 1 shows the typical SEM and TEM images and the SAED pattern. It can be seen that the product presents hexagonal nanodisk morphology with about several microns in diagonal and 100 nm in thickness. Under the TEM, the same SAED patterns were observed for both samples. The TEM image in Fig. 1c reveals that some nanodisks with the size of about 0.4 μ m in diagonal and 50 nm in thickness. The SAED pattern demonstrates that the ZnO nanodisk grows mainly along the six symmetric directions of $\pm [10\overline{1}0]$, \pm [1100] and \pm 0110]. The reported results [8,12] have demonstrated that the nanodisks were formed when the growth along [0001] direction was suppressed through surface chemical modification [12] or high vapor pressure [8]. In present case, the high Zn vapor pressure was supplied by thermal evaporation of Zn powders at about 750 °C and carbon-thermal reduction of ZnO powders at 1000 °C. The growth mechanism of the ZnO nanodisk has been discussed in detail in our previous work [8].

Both sample A and B present a similar XRD pattern, as illustrated in Fig. 2a. As indexed in the figure, all diffraction peaks match with the wurtzite structural ZnO with lattice constants of a = 3.250 Å and c = 5.207 Å. Consistent with the growth direction of ZnO nanodisks, the strong diffraction peaks appear at 31.8°, and 36.5°, which correspond to (1010), and (1011) planes of wurtzite ZnO, respectively. Even so, the difference between these two XRD patterns still can be observed by careful comparison. The main diffraction peaks between 30° and 40° was enlarged in Fig. 2b. It is



Fig. 2. XRD patterns (a) with enlarged parts for 2θ between 30° and 40° (b) of ZnO nanodisk sample A and sample B.

noted that the width of the diffraction peaks for sample A are narrower than that for sample B. This indicates that sample A grown at higher temperature has better crystal quality than sample B grown at lower temperature.



Fig. 1. SEM image of sample A (a), and SEM, TEM images and the corresponding SAED pattern of sample B (b-d).

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