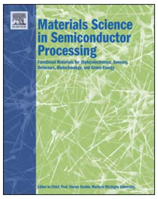
Materials Science in Semiconductor Processing 56 (2016) 127–136

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

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



Effects of high-temperature rapid thermal annealing for seed layers on the crystallographic evolution in hydrothermal ZnO nanostructures

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ARTICLE INFO

Article history:
Received 20 May 2016
Received in revised form
19 July 2016
Accepted 11 August 2016

Keywords:
ZnO seed layer
Nanorods
Rapid thermal annealing
Hydrothermal growth
Crystal orientation
Flower-like morphology
Pioneer crystal

ABSTRACT

In this work, we investigated effects of high temperature rapid thermal annealing for the zinc oxide (ZnO) seed layers on the growth morphology and crystal orientation of hydrothermal ZnO nanorods (NRs). The seed layers were prepared by sol–gel spin coating and annealed by two-step rapid thermal processes at different peak temperatures ranging from 600 to 900 °C for a short time period of 1 min. The seed layers annealed in a temperature range of 600–800 °C were all polycrystalline; however, they exhibited a highly Zn-deficient amorphous state when annealed at 900 °C as observed by X-ray photoelectron spectroscopy, X-ray diffraction (XRD), and cross-sectional transmission electron microscopy (TEM). The vertical NRs normal to the substrate were grown along [001] direction atop the polycrystalline seeds annealed at 600–800 °C, whereas different growth morphology of flower-like NRs was observed on the seeds annealed at 900 °C with the strongest XRD peak along the [100] orientation. From our cross-sectional TEM analysis, this flower-like architecture was initiated from the pioneer crystals laterally grown along [001] direction guiding the subsequent growth of petal NRs oriented by a slight difference in growth direction.

1. Introduction

Zinc oxide (ZnO) has been highlighted as an attractive wide bandgap material of a direct bandgap of 3.37 eV and a high exciton binding energy of 60 meV enabling the excitonic emission processes to persist even above room temperature (RT) [1]. Due to the superior optical properties of ZnO material near ultra violet (UV) spectral region [2], a variety of nanostructures including nanoparticles [3], nanorods (NRs) [4], nanowires [5], and nanoflowers [6] have been investigated extensively for various application purposes depending on their morphology and fabrication method [7]. Among them, the NRs or nanowires have received the greatest attention for their promising applications in electronic and optoelectronic devices [8], such as UV lasers [9], solar cells [10], gas sensors [11], photodetectors [12], light emitting diodes [13], and surface acoustic wave devices [14]. The performances of these devices are deeply associated with the growth of the ZnO nanomaterials aligned to a specific crystal direction with high crystalline quality.

A variety of growth techniques for fabricating the high-quality ZnO nanostructures have been reported to date, such as metal-organic chemical vapor deposition [15], electro-deposition [16], vapor-liquid-solid epitaxy [17], pulsed laser deposition [18], and template-based method [19,20]. Because most of these methods require complex and expensive processes, a low temperature and cost effective method called “hydrothermal growth” has been studied intensively [21] as an alternative growth technique for the ZnO NRs. The hydrothermal growth method requires no catalyst, and it is applicable to the fabrication of uniform ZnO NRs at low temperature on large area substrates [22,23]. In this growth technique, various parameters can affect the morphology and crystal orientation of ZnO NRs as reported in [24]. Especially, the seed layer growth itself significantly affects the density and crystal structure of ZnO NRs. For example, seed layers doped with metals can influence the crystallization, packing density, and c-axis alignment of the ZnO NR as described in [25,26]. A great amount of research effort was made on the seed layer growth technique such as sol–gel ZnO seed layers [27], RF magnetron sputtered ZnO seed layers [28], and spin-coated ZnO nanoparticles [29]. Post-annealing for the seed layers can also significantly affect the growth rate and morphology of ZnO NRs as presented in many earlier studies [30,31].

In this work, we examined the effects of rapid thermal annealing (RTA) for the ZnO seed layers (600–900 °C, for 1 min) on the morphology and crystal orientation of the subsequent hydrothermal growth of ZnO NRs. Process steps of the ZnO NR-based devices are generally limited by the thermal stability up to ~600 °C when glass is used as a transparent low-cost substrate.

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http://dx.doi.org/10.1016/j.mssp.2016.08.006
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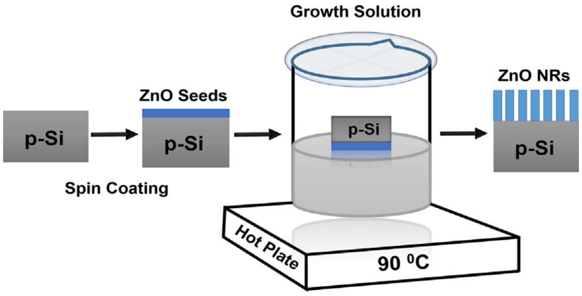

Fig. 1. Schematic of the growth procedure for ZnO nanorods.

However, high-temperature treatment in a short time period can actually improve the structural properties of the NRs and therefore the device performance. Based on the experimental result of the best performance of polysilicon solar cell grown on glass rapid-thermal annealed at a peak temperature of 900 °C for 200 s [32], we chose the annealing condition at a peak temperature of 900 °C for 1 min as a maximum thermal stress in this study. We also investigated the role of crystal structure and the surface morphology of as-annealed seed layers in the growth of ZnO NRs by using various surface characterization techniques including X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), field emission scanning electron microscopy (FE-SEM), photoluminescence (PL), and high-resolution transmission electron microscopy (HRTEM).

2. Experimental procedure

The ZnO NRs were grown by the hydrothermal method in the following procedure. All chemicals used in this study were of analytical reagent grade (procured from Sigma-Aldrich) and used without further purification. For the ZnO seed growth, a solution was prepared using 0.2 M zinc acetate dehydrate in 30 ml 1-prponol with the same concentration of monoethanolamine. The prepared seed solution was aged for 24h to get the sol stabilized. (100) p-silicon wafers ($20 \times 20\ \text{mm}^2$) were used as

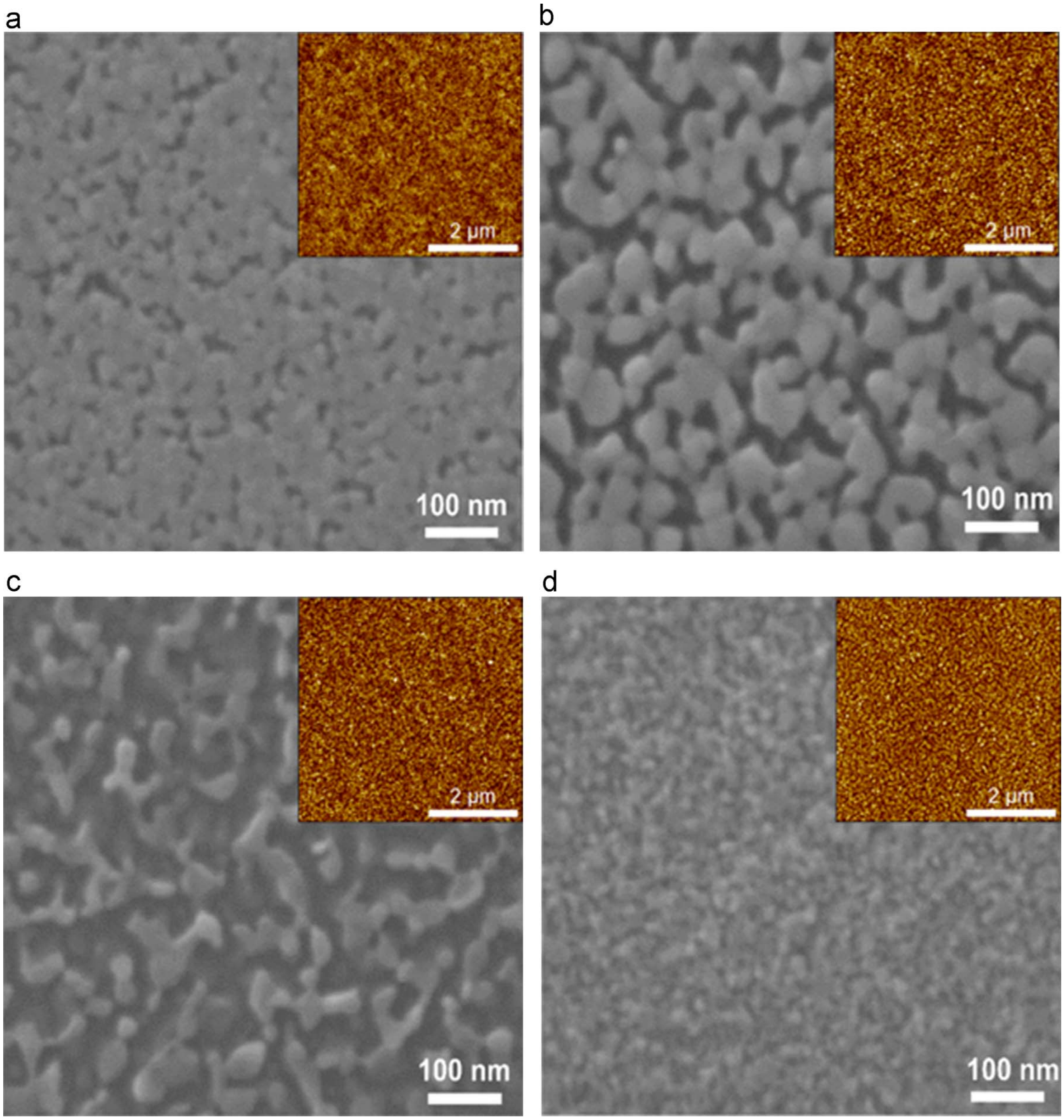

Fig. 2. SEM plane-view images of the as annealed ZnO seed layers at (a) 600, (b) 700, (c) 800, and (d) 900 °C. AFM micrographs of each seed layer were shown in the insets.