Journal of Alloys and Compounds 513 (2012) 180–183

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

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

Position-controlled vertical arrays of single-crystalline ZnO nanowires on periodically polarity inverted templates

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ARTICLE INFO

Article history:
Received 18 July 2011
Received in revised form 3 October 2011
Accepted 5 October 2011
Available online 17 October 2011

Keywords:
ZnO
Polarity
Nano
Array
Template
MBE

ABSTRACT

Position controlled single crystalline ZnO nanowires are grown on periodically polarity-inverted (PPI) ZnO heterostructures without catalyst. PPI ZnO templates were fabricated by using selective growth method of polarity with Cr-compound intermediate layers by plasma assisted molecular beam epitaxy. In order to control the position, we used the in-plane two-dimensionally discrete PPI ZnO templates. The lateral polarity inversion in PPI template was confirmed by piezo response microscopy. After syntheses of ZnO nanowires, vertically aligned ZnO nanowires were grown only onto the Zn-polar regions without the O-polar regions. The results clearly show that the position control of ZnO nanowires is possible using the PPI ZnO templates.

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1. Introduction

One-dimensional (1D) nanostructures have attracted considerable attentions for the past decades as building blocks for photonics and electronic nanodevices [1–3]. Among compound semiconductor nanomaterials, ZnO nanowire is a representative oxide semiconductor material with versatile application fields such as solar cell [4], chemical and biological sensing [5,6], optoelectronics [7], energy conversion [4], and field emission [8]. In order to integrate of nanodevices grown on various substrates, the growth of the nanowires in the desired area is required. The position controlled ZnO nanostructures are very useful to be used as a functional component in nanoscale photonic devices [9]. Although a few well controlled compound semiconductor nanowires with or without the catalyst are reported, catalyst free position controlled growth of oxide nanomaterials are not so many demonstrated [10,11]. Intensive efforts for the growth of well aligned ZnO nanostructures have been successfully achieved on various substrates via a vapor–liquid–solid (VLS) mechanism [12,13] using catalyst seeds used for promotion of nanowires growth. But remained metal catalyst after synthesis process may contaminate the target nanomaterials and usually act as impurities which degrade the material properties including optical and structural and finally harmful to device level applications [14,15]. In addition, the use of catalyst for the VLS process based on the supersaturation in catalyst make the migration and diffusion of metal atoms into the source materials or substrate, which can make it difficult to control the position and materials properties [16].

Therefore, recently, some efforts are conducted for the growth of vertically aligned ZnO nanorods using the template-assisted growth [5] and electrical field alignment without the any catalyst [17]. Even though the expansion to the periodical two-dimensional (2D) ZnO nanostructures from 1D has potential applications in various lateral optical and electrical devices, few studies about them have been reported [18].

ZnO crystallizes in a wurtzite structure and naturally has crystal polarity along the *c*-axis. Due to the differences of material properties depending on the polarity, various methods are suggested to control the polarity of ZnO films on *c*-sapphire substrates [19–21]. Until now, the polarity control itself has been extensively studied, but the spatial array and applications are not so many reported [22]. Here, we would like to emphasize that periodically polarity-inverted (PPI) ZnO heterostructures can be used as a template for position controlled ZnO nanostructures without catalyst.

CrN used in our experimental has many advantages for the growth of GaN and ZnO because the lattice constant and thermal expansion coefficient of rock-salt CrN layer lie in between those of wurtzite compound semiconductors and *c*-sapphire [22,23]. In terms of the formation of CrN, there are versatile mechanisms using the nitridation of Cr-metal layer and direct growth of CrN using the

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doi:10.1016/j.jallcom.2011.10.015

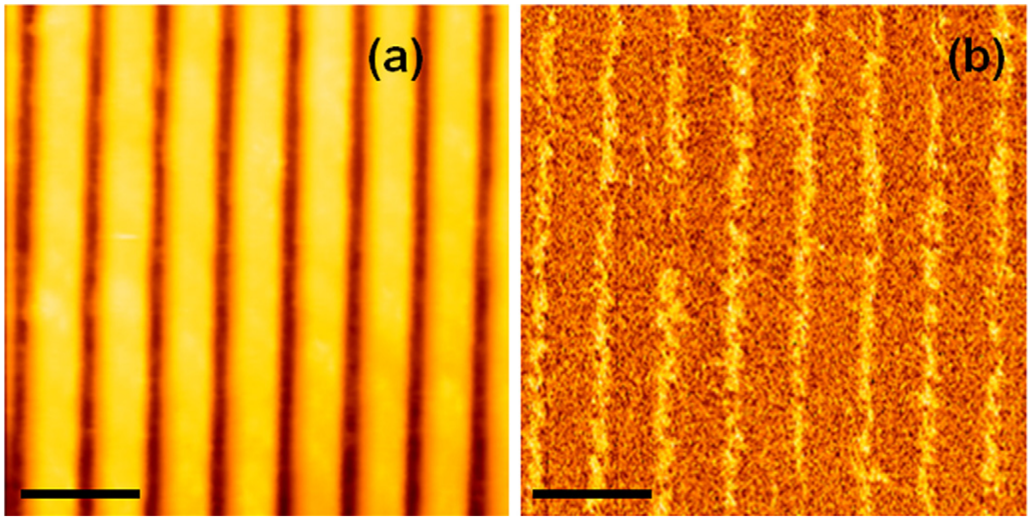

Fig. 1. (a) AFM and (b) PRM images of PPI ZnO templates formed on *c*-sapphire substrate.

MBE system [23,24]. In the case of the CrN growth the growth range is very wide which means that we can easily growth the high quality CrN. In addition, the pattern formation is very easy using the selective etching by Cr-etchant [25,26].

In this paper, we report the realization of a vertically aligned 1D ZnO nanowires on PPI ZnO heterostructures, which were fabricated using previously proposed in situ polarity control methods [21]. This approach will open the possibility of creating patterned mutidimensional nanostructures for applications as optoelectronics, sensors, and nonlinear optical devices.

2. Experimental details

In order to fabricate the PPI ZnO templates on c-Al_2O_3 substrate, we used the in situ polarity control methods using the Cr compound buffer layers. The details for the selection of polarity of ZnO and fabrication methods are can be found elsewhere [22].

The ZnO nanowires on PPI ZnO templates were grown by chemical vapor transport and condensation method using carbothermal reduction of ZnO powder in furnace. A mixture of equal amounts of ZnO (99.999%, Sigma–Aldrich) and graphite (99.9%, Sigma–Aldrich) powder was used as a Zn source. The source boat was placed at the center of the quartz reactor equipped with the inner tube. The mixture gas made of argon (95%) and oxygen (5%) was used as an oxygen source. The reactor was heated to the set temperatures and maintained at 900 °C for the specific growth time. The produced ZnO nanowires were characterized by scanning electron microscopy (SEM: JEOL) and high resolution X-ray diffraction pattern (HR XRD, Phillips Cu-Kα radiation). The optical properties of the ZnO nanowires grown on PPI ZnO template were measured at room temperature using a photoluminescence (PL) with a 325 nm He–Cd excitation source.

3. Results and discussion

To elucidate the periodical polarity inversion in the fabricated structures, we conducted piezo response microscopy (PRM) measurements using an atomic force microscopy (AFM, SPA400). Fig. 1(a) shows the AFM image of PPI ZnO template surface showing the 1D patterning with 500 nm period, and the contrast observed in the figure results from the difference in the heights of the Zn- and O-polar regions, which is related to the difference of growth rate depending on the polarity. In the case of PPI ZnO heterostructure, the growth rates of Zn- and O-polar ZnO are different; as a result, a step height is formed, whose magnitude depends on the growth conditions of the PPI ZnO structure [21].

The PRM technique has been successfully used to determine the polarity of ZnO film with patterned Zn and O polarities at the micrometer scale [22]. The ZnO films can expand along the [0 0 0 1] axis with a positive electric field and contract when the direction of the electric field is reversed; the contrast in PRM image shows this expansion and contraction effects. The image of the piezoelectric response of the fabricated PPI structure clearly shows both regions with different brightness, as shown in Fig. 1(b). Here, the bright and dark regions correspond to the O-polar and Zn-polar films, respectively. The PRM images and piezo response curves (not shown here) can be considered clear evidences for the polarity inversion in the PPI ZnO structures with nanometer scale period.

Fig. 2 shows the position-controlled vertical arrays of ZnO nanowires on PPI ZnO templates. Fig. 2(a) and (b) shows low magnification and high magnification top view of ZnO nanowires, respectively. Two or three white spots are shown in the each island which is related to the Zn-polar regions formed in plane discrete PPI ZnO templates. All of the ZnO nanowires have almost the same height of about 6 μm and their diameters range between 80 and 120 nm. It clearly demonstrates that most of the ZnO nanowires grow perpendicular to the substrate. Moreover, those are grown on the Zn-polar ZnO regions without on the O-polar regions. We want to find out the possible mechanism from the self-catalyzed effect on Zn-polar region which was suggested by Wang et al. They previously reported the different growth characteristics of ZnO nanoribbon using different polar surface [27]. They concluded that Zn-polar surface is chemically active possibly due to self-catalyzed process in growth of ZnO, while the O-polar surface is chemically inert. Therefore, the ZnO nanowires can be preferentially grown on discrete Zn-polar regions on templates with 500 nm scale pattern size.

In order to investigate the structural properties including the epitaxial relationship and crystallinity of ZnO nanowires on PPI ZnO structures, a HR XRD machine was used. Fig. 3(a) shows the XRD θ–2θ scan data of the position controlled array of ZnO nanowires. These spectra can be indexed to ZnO (0 0 0 2), CrN (1 1 1), and Al_2O_3 (0 0 0 6) for diffractions peaks at 34.48°, 38.02°, and 41.70°, respectively. Typical full width at half maximum of rocking curves data obtained from the (0 0 0 2) peak of the as-grown ZnO nanostructures were between 0.2 and 0.3°. In addition, as shown in Fig. 3(b), six equidistant narrow peaks of the ZnO $(1 0 \bar{1} 1)$ plane are observed in the Φ-scan range of 0–360°, which is indicative of the growth of good crystallinity and vertical alignment of the nanowires on the PPI substrate without the rotational domains.

In order to collect optical properties of the vertical aligned ZnO nanowires on PPI ZnO, PL spectra were acquired from the ZnO nanowire arrays. Fig. 4 shows the PL spectra of the ZnO

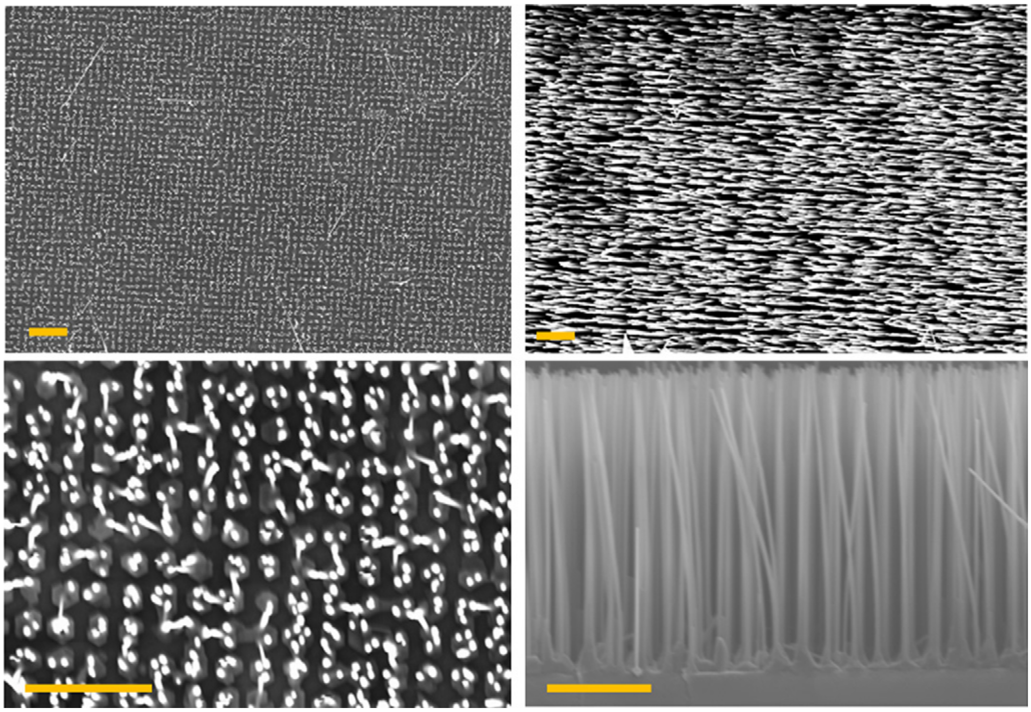

Fig. 2. (a) Low magnification top-view SEM image of 2D aligned ZnO nanowires grown onto 2D PPI ZnO. (b) The magnification of (a). (c) Tilted images of the aligned ZnO nanowires at an angle of 30°. (d) Aligned ZnO nanowires at the edge of the growth pattern. Scale bar indicates the 2 μm.

nanowire obtained at 10 K. Strong near band edge emission in the UV range and negligible week green emission were observed. Two peaks at 3.360 and 3.374 eV can be assigned to D^oX and FX associated with neutral donor-bound and free exciton recombination, respectively [28]. Surface exciton related emission also clearly appeared at 3.368 eV which indicates that the ZnO nanostructure has a large surface to volume ratio [29]. The peak at 3.321 eV with the strongest intensity corresponded well with the reported position for a free-electron-to-bound-hole (eA^0) [30]. This peak was observed in ZnO films on Cr-compound related buffer layers [21]. Two emission lines in the low energy part, at around 3.29 eV and 3.22 eV, are assigned to phonon replica of D^oX with 71 meV spacing, respectively.

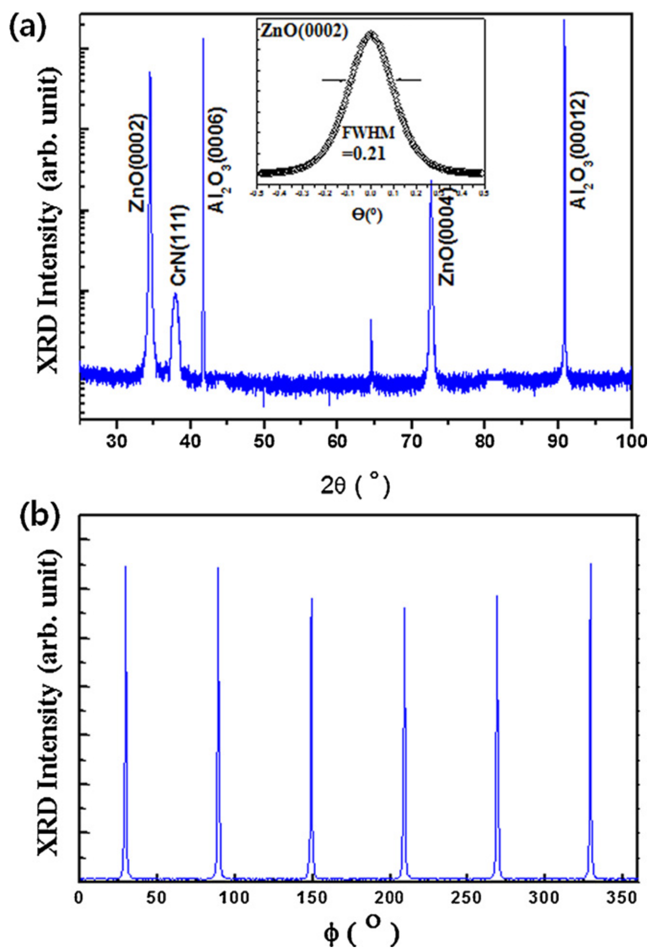

Fig. 3. X-ray diffraction (a) θ–2θ scan, (b) Φ-scan spectra of (1 0 −1 1) planes of the as-grown ZnO nanowire arrays on the PPI ZnO template. Inset of (a) shows the typical ω-rocking curve of the (0 0 0 2) ZnO plane.

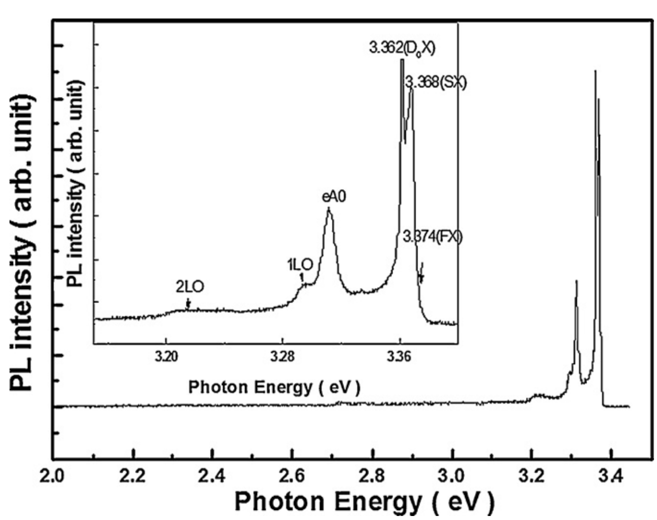

Fig. 4. 10 K PL spectra of the vertically aligned ZnO nanowires grown on PPI ZnO templates. The inset shows a detail of the near band edge emission.

4. Conclusions

In conclusion, we present the fabrication methods of catalyst free position controlled ZnO nanowires on PPI ZnO templates on (0 0 0 1) Al_2O_3 substrate. In order to prepare the PPI ZnO, the periodical polarity inversion method based on in situ polarity control is used. The well aligned nanowires can be grown on the only Zn-polar regions which makes selective growth of ZnO nanowires on desired regions. In general, we believe that this approach using periodical array of ZnO templates will open the possibility of the other expended well-aligned hybrid nanostructures for optoelectronics, photonic crystal, sensor arrays, and nonlinear photonic crystals.

Acknowledgment

This work was supported by the research fund of Hanyang University (HY-2011-00000000229).

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