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Laterally grown ZnO nanorod arrays on an obliquely deposited seed layer and its UV photocurrent response

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ABSTRACT

Laterally grown ZnO nanorods have advantages over vertically grown ones in terms of process complexity in ultraviolet photodetector fabrication. A ZnO seed layer was deposited on a glass substrate by an oblique-angle sputtering method and Cr thin film was deposited and patterned as the metal contact with the ZnO nanorods. Cr lines also acted as a growth barrier to suppress vertical ZnO growth. Oblique sputter deposition of ZnO thin films resulted in an inclined columnar growth, and the ZnO nanorods were grown laterally and unidirectionally by a Cr growth barrier in a hydrothermal bath. With 80° oblique deposition, the c-axis of the ZnO seed layer inclined by 5° from the vertical direction. The photocurrent of the detector in 365 nm illumination increased by 100 times over that of the dark current. Passivation of the ZnO nanorod surface by polydimethyl siloxane (PDMS) showed an even higher photocurrent.

1. Introduction

In recent years, ZnO nanorod structures have been widely used in photonics applications such as UV sensors or light-emitting diodes [1]. In UV sensor applications photoconductivity change of ZnO nanorods upon UV light exposure is utilized. They typically have a metal–semiconductor–metal (MSM) structure, where ZnO nanorods are grown to fill gaps of interdigited metal electrodes [2–10]. ZnO nanorods or nanowires can be grown vertically or horizontally on various substrates with a ZnO seed layer by various methods, such as thermal evaporation [5,6], vapor–liquid–solid method [7], or hydrothermal method [2,3,8–11]. In this work, the hydrothermal method is used because it has several advantages: low cost, low temperature process, and simple set-up. For vertical MSM structures made of vertically grown ZnO nanorods, more process steps are needed to make a top electrical contact after the ZnO nanorods are grown [4]. Therefore, there have been efforts to develop a simpler method to make sensors with a horizontal MSM structure, which requires laterally grown ZnO nanorods. For lateral growth it is necessary to form metal blocking layers of such as W, Ni, Sn, Cr or Ti/Pt to prevent vertical growth [5,9–12], or Au catalyst [13]. These metal blocking layers are inactive to ZnO growth and also act as metal electrodes for the sensor. In a hydrothermal bath, ZnO nanorods have been grown from both sides of metal blocking layers, which results in networked structures, interlinking nanorods and growth barriers [9–11].

In this paper, a novel method by which ZnO nanorods are grown laterally from only one side of the ZnO seed layer is proposed. For growing ZnO nanorods from only one side of the seed layer, shielding of the growth site by metal layer has been tried [12]. In this work, we have grown ZnO nanorods laterally and unidirectionally using the metal blocking layer and inclined columnar ZnO seed layer. The MSM structure fabricated by this method was tested in terms of UV photocurrent responses.

2. Experiment

300 nm thick ZnO seed layers were deposited on glass substrates by RF magnetron sputtering of 99.99% pure ZnO target. RF power was 200 W and Ar gas pressure during deposition was 6.7 Pa. The distance between the centers of the target and the glass substrates was kept at 7.0 cm. The substrates were kept at room temperature and tilted by 0°, 30°, 60° and 80° from the normal direction of the sputtering beam, respectively. Next, 80 nm thick and 3 μm wide Cr lines were prepared by a lift-off method. The samples were then placed in a 0.001 M HCl solution and ZnO seed film uncovered by Cr line was etched away and the ZnO seed layer underneath the Cr line remained as shown in Fig. 1. Because of isotropic wet etching, the ZnO layer was over-etched and under-cut and the Cr layer acted as a vertical growth barrier as shown in Fig. 1. ZnO nanorods were then grown in a 0.03 M solution of zinc nitrate hexahydrate [$Zn(NO_3)_2{\cdot}6H_2O$] and Hexamethylenetetramine (HMT) [$C_6H_{12}N_4$] at 70 °C. The process steps to make the lateral metal–semiconductor–metal (MSM) structure were basically same as in the previous reports [9–12]. Field emission scanning electron microscope

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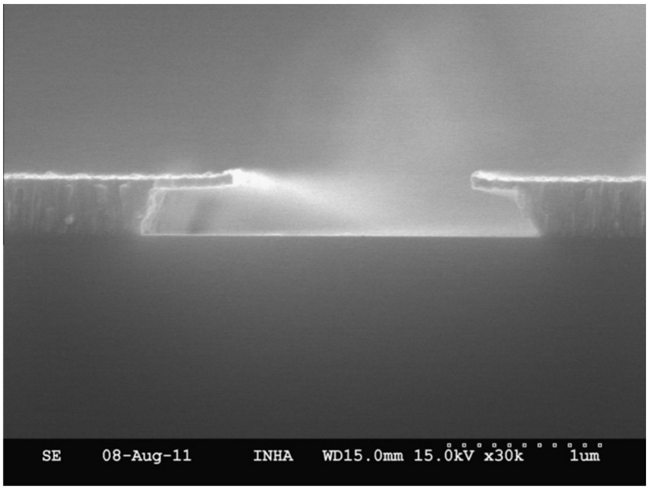

Fig. 1. Cross-sectional SEM image of MSM structure just before hydrothermal growth. The ZnO seed layer was over-etched underneath the Cr metal lines.

(FESEM) (Hitachi S-4300) was used to observe the morphology, and X-ray diffraction to check the crystallinity of the ZnO seed layers and ZnO nanorods. The ZnO nanorod surface was coated with polydimethyl siloxane (PDMS) to check the validity of the surface passivation effect. The optical response of the MSM detector was measured by photoluminescence spectroscopy (Micro-PL System by Dongwoo Optron) and the photocurrent–voltage (I–V) characteristics was measured under UV exposure.

3. Result and discussion

XRD showed that all the ZnO seed films deposited on glass regardless of the tilting angle had peaks at 34.3°, 31.4° and 36.2°, which is assigned as (002), (100), and (101), respectively. Cross-sectional SEM images of the ZnO seed films revealed columnar growth. For the ZnO films deposited at 80° tilting angle columnar growth was tilted toward the incident angle of the sputtered particles by 5° with respect to the surface normal as shown in Fig. 2. However, the other ZnO films deposited at different angles of 0°, 30° and 60° showed no inclined columnar growth in the cross-sectional view.

It has been reported that oblique sputter deposition of ZnO thin films on glass [14,15] or Si(100) wafer [16,17] caused the inclination of columnar structure or c-axis toward the incident angle of sputtered particles. In some cases only XRD observation showed the inclination of the c-axis [14,16] and in other cases both cross-sectional micrograph and XRD data indicated the inclinations [15,17]. In case of glass substrates only those deposited at higher tilt angles than 60° [14] or 80° [15] showed the inclinations. It has been regarded that adatom mobility arriving at substrate becomes higher for larger oblique deposition and that when incoming sputtered particles obliquely arrive at the substrate they prefer the nucleation of tilted islands and tilted grain growth. If the substrates have crystalline facet it would be easier to get inclined c-axis growth for all oblique angle of deposition [17]. However, in case of glass substrates even larger oblique angle is required to get the inclined growth [15], which is the same observation with this work. It might be the results of combination of vertical growth and oblique arrival of adatoms.

Fig. 3 shows an early stage of ZnO nanorod growth and the nanorods grew laterally because of metal blocking layer [9–12]. XRD shows the strong (002) peak from the nanorods and their hexagonal cross section implies c-axis is along their growth direction. The lateral growth suggests that nucleation took place only at the open area exposed to the edge of ZnO seed layer and that c-axis of ZnO nanorods pointed laterally [9,12]. The growth from both sides as in Fig. 3a was observed for the seed layers deposited at 0°, 30° and 60°. However, growth of the nanorods from the ZnO seed layer deposited at 80° was from only one side as shown in Fig. 3b. This result suggests that the inclined columnar structure

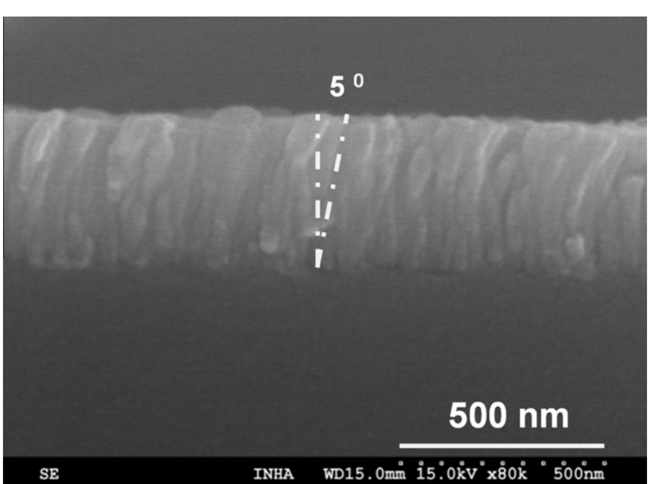

Fig. 2. Cross-sectional SEM image of inclined columnar growth of ZnO seed layer.

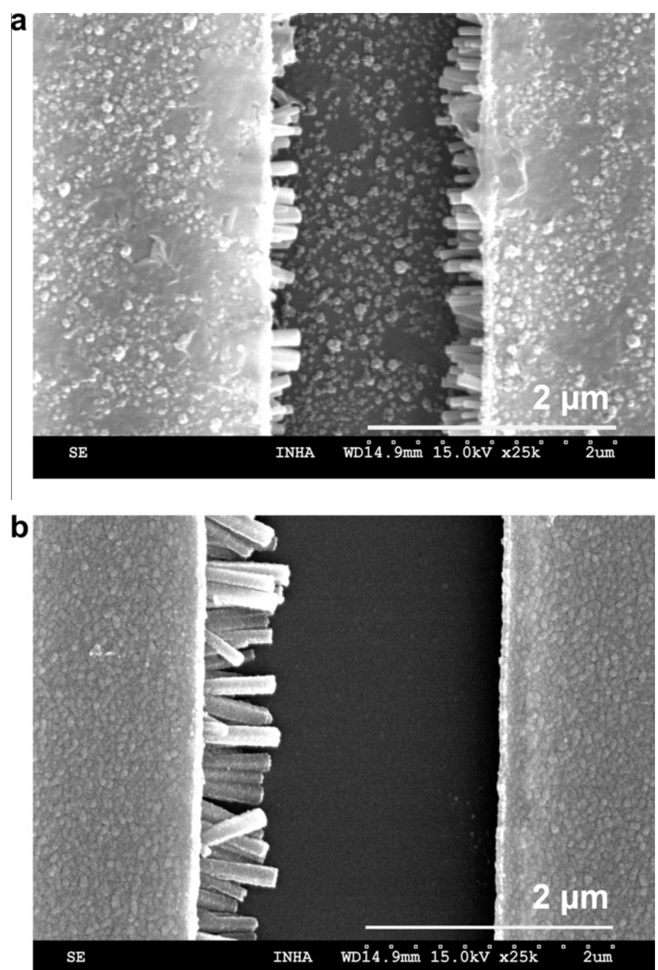

Fig. 3. SEM images of ZnO nanorods grown laterally. (a) Seed layer was deposited at 0° oblique angle, and (b) seed layer was deposited at 80° oblique angle.