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Effect of surface preparation on the morphology of ZnO nanorods

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Abstract

The effects of Si substrate orientation and surface treatment on the morphology and density of Zinc oxide (ZnO) nanorods were investigated. The size and density of ZnO nanorods were influenced by Si substrate orientation and surface preparation. ZnO nanorods synthesized on the ideally H-terminated Si(1 1 1) prepared with an NH_4F solution resulted in the biggest size and the lowest density. It is suggested that the smoother surface of the Si substrate and lattice shape match with a larger atomic distance result in the increase of the ZnO seedlayer's grain size, which in turn enhances the size of ZnO nanorods grown on it. The optical properties of the ZnO nanorods were affected by their size and crystallinity. The smallest ZnO nanorods with a preferential *c*-axis orientation synthesized on the HF-treated Si(1 1 1) surface showed the highest intensity ratio of UV to visible emission, and the biggest ZnO nanorods synthesized on the N_2-sparged NH_4F-treated Si(1 1 1) surface showed the lowest intensity ratio of UV to visible emission. Therefore, it can be concluded that Si substrate orientation and surface preparation significantly affect the optical properties of ZnO nanorods.

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Keywords: ZnO nanorods; Orientation; Si surface; Photoluminescence

1. Introduction

Zinc oxide (ZnO) is a II–VI semiconducting material having a wurtzite hexagonal structure, with lattice parameters $a = 3.2501$ Å, $c = 5.2066$ Å [1]. The Zn^{2+} ion of a ZnO crystal is surrounded by four O^{2-} ions, and the ZnO crystal has a polar surface. The structural property of ZnO crystals contributes to its rapid growth toward a $\langle 0001 \rangle$ orientation; thus nanorods are more easily synthesized than other materials [2,3]. The morphology and crystallinity of synthesized ZnO nanorods affect both their optical and electrical properties [4,5]. For example, as ZnO nanorods shrink, the intensity ratio of UV emissions to visible emissions (I_{UV}/I_{vis}) increases [4]. When flower, snowflake, and prickly spherical ZnO nanostructures were formed from $ZnAc_2$, the intensity of UV emission was highest for the snowflake type and lowest for the prickly spherical type [5]. Therefore, morphology and crystallinity must be controlled to effectively fabricate nanodevices using ZnO nanorods.

In synthesizing ZnO nanorods with hydrothermal solutions, their morphology is changed by pH, reaction temperature, and the additives of the precursors [6–11]. With an increased concentration of the Zn^{2+} precursor, length and diameter of ZnO nanorods increases [6]. It is reported that length and diameter of ZnO nanorods increase when pH of the synthesis solution increases from 8.8 to 9.7 [7]. The morphology of ZnO nanorods changes when reaction temperature is increased from 40 to 95 °C, [8]. If $Fe(CH_3COO)_2$ is added to the synthesis solution to dope Fe in the ZnO nanorods, the density of the ZnO nanorods is decreased without a remarkable change in their size [9]. As stated, various experiments with the hydrothermal solution method affected the morphology and density of ZnO nanorods.

In addition, it is reported that the seedlayer affects the morphology of ZnO nanorods [10,11]. Well-aligned ZnO nanorods perpendicular to the substrate do not grow easily without a seedlayer. However, when a ZnO crystal is

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formed as the seedlayer, ZnO nanorods grow easily [10]. It is also known that the $\langle 0001 \rangle$ orientation of a ZnO seedlayer is strongly related to the growth rate of ZnO nanorods [11].

The hypothesis of this paper is that the thin-film seedlayer that affects the growth of ZnO nanorods can be influenced by the surface condition of the Si substrate. In the case of the ideally H-terminated Si(1 0 0) substrate, the square type of face-centered plane is repeated, although the atoms on the face are not directly bonded to each other. The H-terminated Si(1 0 0) surface has mono-, di-, and tri-hydrides thus the surface is atomically rough. On the other hand, the ideally H-terminated Si(1 1 1) surface treated with the O_2-free NH_4F solution reveals mono-hydrides, [12] mainly with hexagonal planed atoms. Therefore, surface orientation and roughness of the Si may affect the structure of ZnO thin-film seedlayer, which is deposited on the Si surface. Consequently, surface condition of Si can affect the morphology of ZnO nanorods. Therefore, in this paper, the effect of Si substrate orientation and surface treatment on the morphology and density of ZnO nanorods is discussed.

2. Experimental

p-Type Si(1 1 1) and p-type Si(1 0 0) wafers were used in this study. Pieces of wafer were treated in HF or NH_4F solution to remove the natural oxide layer. One ml of a 49% HF solution (J.T. Baker) was diluted in 100 ml of deionized water. Si(1 1 1) and Si(1 0 0) substrates were dipped in the diluted HF for 5 min to prepare for hydrogen termination. In order to remove dissolved oxygen in a 40% NH_4F solution (J.T. Baker), N_2 gas was injected into 50 ml of NH_4F solution for 15 min. Then, the Si(1 1 1) substrate was dipped in the NH_4F solution for 5 min to prepare a pit-free H-terminated Si(1 1 1) surface.

Right after the surface treatment of the Si substrate in HF or NH_4F solution, the ZnO seedlayer was deposited by RF sputtering using a ZnO target. The working pressure was 1.0×10^{-3} torr, the Ar flow rate was 20 sccm and RF power was 80 W. The thickness of the ZnO seedlayer was 20 nm.

The ZnO nanorods were created using low-temperature hydrothermal synthesis. 0.7139 g of $Zn(NO_3)_2 \cdot 6H_2O$ (98% purity, Aldrich) was dissolved in 80 ml of deionized water. Then, NH_4OH (28% purity, Junsei) was added to set the pH of the solution at 10.3. The synthesis was performed at 60 °C for 30 min. After the synthesis reaction, the samples were taken out of the solution, rinsed with deionized water, and dried.

Fourier transform infrared spectroscopy (FT-IR, Thermo, Nicolet 380) was used to observe the state of the Si surface, such as termination and microroughness. For the Si(1 0 0), a multi-internal reflection (MIR) FT-IR was taken by fabricating a 45° beveled trapezoidal $80 \times 10 \times 0.65$ mm Si(1 0 0) wafer piece. A Brewster angle (73.75°) transmission FT-IR spectra was used to measure hydrogen termination on the Si(1 1 1) substrate, suppressing reflection and maximizing p-polarized information. Atomic force microscopy (AFM, Seiko Instrument, SPA-400) was used to observe surface morphology of the ZnO seedlayer. The crystallinities of the seedlayers and nanorods were measured by X-ray diffraction (XRD, Rigaku D/MAX-2500 H). The morphologies of ZnO nanorods were observed using a field-emission scanning electron microscope (FESEM, Hitachi S-4200). The photoluminescence spectra (PL, SPEX1403) was measured to investigate the optical properties of the ZnO nanorods.

3. Results and discussion

3.1. Effect of Si surface on the morphology and the optical properties of ZnO nanorods

The SEM images of ZnO nanorods grown on various Si surfaces are shown in Fig. 1. The ZnO nanorods were vertically aligned on the Si substrate with a hexagonal wurtzite structure. However, the size and density of nanorods per unit area were influenced by the surface condition of the Si substrate. The diameters and numbers of nanorods obtained from SEM images are summarized in Fig. 2. The diameter of the ZnO nanorods grown on the Si(1 1 1) substrate treated with O_2-free NH_4F solution was 2.3 times larger than those grown on the Si(1 0 0) substrate treated with the HF solution, and the number of nanorods was 6.7 times smaller.

XRD patterns of ZnO nanorods grown on various Si surfaces are shown in Fig. 3. In all cases, dominant *c*-axis

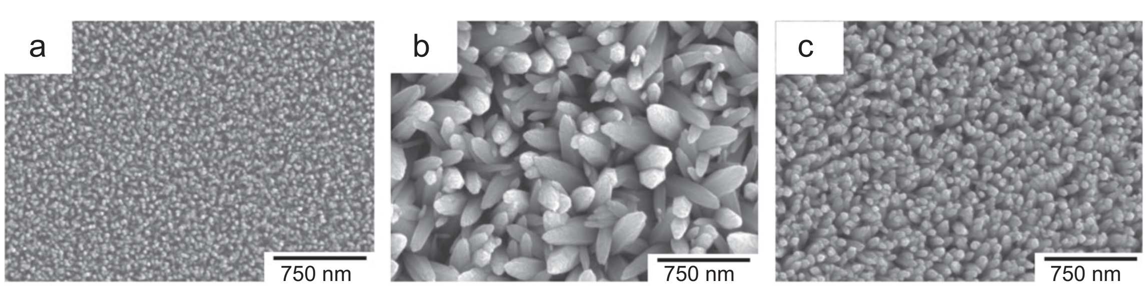

Fig. 1. SEM image of the ZnO nanorods grown on each Si surface. (a) Si(1 0 0) treated with an HF solution, (b) Si(1 1 1) treated with an N_2-sparged NH_4F solution, and (c) Si(1 1 1) treated with a HF solution.