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Effect of ZnO seed layers on the solution chemical growth of ZnO nanorod arrays

Sea-Fue Wang *, Tseung-Yuen Tseng, Yuh-Ruey Wang, Chun-Yun Wang, Hsi-Chan Lu

Department of Materials and Mineral Resources Engineering, National Taipei University of Technology, Taipei, Taiwan, ROC

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Abstract

High density ZnO nanorod arrays were grown on Si substrates coated with ZnO seed layers via aqueous solution route. The ZnO seed layers were deposited on the substrate using DC reactive sputtering and RF magnetron sputtering. It was found that ZnO seed layer with (1 0 3) preferred orientation, prepared using DC reactive sputtering, did not facilitate the formation of ZnO nanorods in the solution grown process. Prior seeding of the surface by ZnO layer with (0 0 2) preferred orientation, deposited using RF magnetron sputtering, leads to nucleation sites on which ZnO nanorod arrays can grow in a highly aligned fashion. ZnO nanorods with well-defined hexagonal facets (0 0 2) were grown almost vertically over the entire substrate. The uniformity and alignment of the nanorod arrays are strongly related to the properties of underneath ZnO seed layers.
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1. Introduction

ZnO is a chemically and thermally stable n-type semiconductor with a large exciton binding energy of 60 meV and a large bandgap energy of 3.37 eV at room temperature [1]. ZnO nanostructures have been widely investigated for their electrical, photoelectronic, catalytic, and photochemical properties such as ultraviolet (UV) laser diodes, UV optical detectors, optical switches, dye-sensitized photovoltaic cells, dimensionally stable anodes (DSAs), hydrogen storage devices, bio- and gas-sensors [2,3]. To fulfill the demands of high efficiency and activity in numerous applications, high porosity, large surface-to-volume and length-to-diameter ratios, and possible quantum confinement effects are generally required. Up to date, synthesis of one-dimensional (1D) ZnO nanostructures, including nanowires, nanorods, nanobelts, nanopropellers, and nanocages, have been demonstrated via thermal evaporation, vapor–liquid–solid epitaxial (VLSE) mechanism, metal–organic chemical vapor deposition (MOCVD), pulsed laser deposition (PLD), molecular beam epitaxy, templating with anodic alumina membranes, epitaxial electrodeposition, and hydrothermal method [4,5]. Recently, aqueous chemical growth method has been widely investigated for producing ZnO nanorods on various substrates including amorphous, single crystalline, polycrystalline, and flexible substrates [5–11]. Though the chemical methods have been widely proved to be simple, economic and suitable for large scale production, the characteristics of ZnO nanostructures, including diameter distribution, orientation, and aspect ratio, prepared using chemical methods may not be as controllable as those fabricated from vapor phase methods [12,13]. Recently, several studies have grown highly oriented ZnO nanorods, via two-step process, on substrates with the use of preexisting textured ZnO seeds such as a ZnO nanoparticle layer, ZnO films, or surface modification [14–27]. In this study, highly oriented nanorods of crystalline ZnO were successfully synthesized through aqueous solution method at low temperatures (<80 °C) under ambient pressure. ZnO nanorods on various sputtered ZnO seed layers

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* Corresponding author. Present address: Department of Materials and Mineral Resources Engineering, National Taipei University of Technology, No. 1, Section 3, Chung-Hsiao E. Road, Taipei, Taiwan, ROC.
Tel.: +886 2 2771 2171x2735; fax: +886 2 2731 7185.
E-mail address: sfwang@ntut.edu.tw (S.-F. Wang).

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were prepared in the solutions, without the use of a high temperature annealed seeding layer. The effect of crystal orientation of the seed layers on the morphology and crystallinity of the solution grown nanorods are discussed.

2. Experimental procedure

ZnO nanorods have been grown on ZnO seeded silicon wafer ($\rho = 3.3–7.3\ \Omega$ cm). ZnO seed layers were deposited on the silicon wafers (2 in. in diameter) using DC reactive sputtering and RF magnetron sputtering depositions, with targets of Zn metal and ZnO ceramic, respectively. Prior to the use, the silicon substrates were first cleaned ultrasonically for 10 min in acetone and rinsed in hydrogen peroxide (H_2O_2), hydrofloride, and then DI water to remove any impurity and oxide layer. For sputtering, argon and oxygen were used as the working gases with at least 99.995% purity. Prior to deposition, the target was sputter-cleaned. Films were sputtered onto (1 0 0) silicon wafer without any intentional heating. Nominal film thickness is around 600 nm. Details of the sputtering conditions are summarized in Table 1.

ZnO nanorods were grown by an aqueous chemical method in 100 ml of aqueous solution containing 0.04 M zinc nitrate hexahydrate (99%; Showa) and 0.008 M hexamethylenetetramine ($C_6H_{12}N_4$; HMTA; 99%, Acros) in a sealed beaker. The solution was preheated to a constant temperature in a water bath. Then the seeded substrates were immersed at the bottom of the beaker and kept at a constant temperature of 75 °C for 1 h. ZnO nanorod fabrication was performed on wafers having different types of ZnO seed layers by suspending the wafers upside down in the solution. Slight mechanical stirring at a speed of 80 rpm was maintained throughout the entire process. After the reaction, the substrate was rinsed with DI water and dried in air, to remove any residual salts and organic materials, for further characterization.

The nanorods grown on the substrate were subjected to XRD analysis (XRD, Siemens D5000), using a thin film diffractometer with monochromatic Cu Kα radiation, to examine the crystallographic evolution of nanostructure, facilitating the identification of crystallized phase. Scanning electron microscopy (SEM, JOEL JSM-T330A) and energy dispersive spectroscopy (EDS) on the film surfaces were used to characterize the morphological microstructures. In addition, a JEOL-2010 high-resolution transmission electron microscope (HRTEM) operating at 200 kV was used to examine the crystallography and microstructure of the as synthesized nanorods.

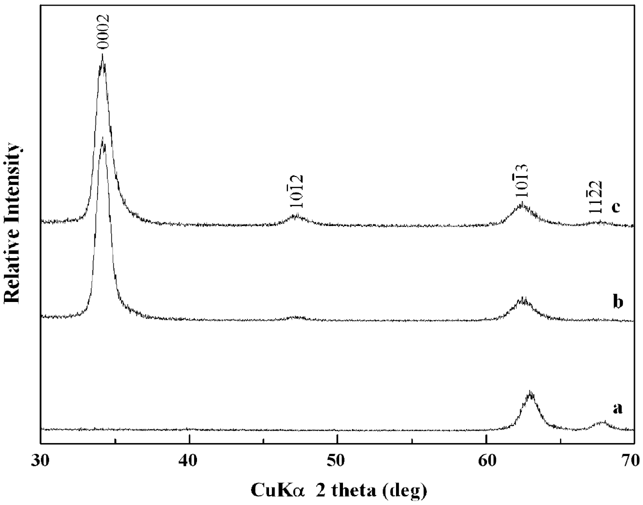

Fig. 1. XRD patterns of different ZnO seed layers covered on Si substrates: (a) ZnO-A seed layer, (b) ZnO-B seed layer, and (c) ZnO-C seed layer.

3. Results and discussion

3.1. Characteristics of various ZnO seed layers

Fig. 1 shows the XRD patterns of various ZnO seed layers, prepared using different methods, covered on Si substrates. Diffraction peaks in XRD patterns for all ZnO seed layers can be indexed as wurtzite hexagonal structure (JCPDS card No. 36-1451, $a = 0.325$ nm and $c = 0.521$ nm). All three ZnO seed layers have thickness around 600 nm. ZnO-B and ZnO-C seed layers have a better crystallinity compared to ZnO-A seed layer according to their peak intensities and widths. The intensities of (1 0 3) peak in ZnO-A and (0 0 2) peak in ZnO-B and ZnO-C are very strong compared with those of other peaks, which provide the evidence that ZnO-A film has a preferred orientation along [1 0 3] direction and ZnO-B and ZnO-C seed films have preferred orientation along [0 0 2] direction (c-axis). Fig. 2 shows the plane view and cross-sectional view of various ZnO seed layers. As seen, ZnO-A seed layer is an amorphous-like film with a smooth surface deposited on the Si substrate. ZnO-B and ZnO-C are highly textured films and have large columnar grains. The surface roughness and crystallinity of ZnO-C seed layer are larger than those of ZnO-B, resulting from the higher working power applied during film sputtering.

ZnO nanorods were grown on various sputtered ZnO seeded substrates. All samples were grown simultaneously in an aqueous solution, containing 0.05 M of $Zn(NO_3)_2$ and 0.01 M of $C_6H_{12}N_4$, in a sealed beaker at a constant temperature of

Table 1
Methods used to grow different ZnO seed layers on Si substrates.

ZnO Film	Method	Target material	$Ar:O_2$	Working pressure (torr)	Power (W)
ZnO-A	DC reactive sputtering	Zn	1:1	1×10^{-3}	400
ZnO-B	RF magnetron sputtering	ZnO	7:3	1×10^{-2}	150
ZnO-C	RF sputtering	ZnO	7:3	1×10^{-2}	175

Sputtering processes were performed at room temperature without the heating of the substrate.

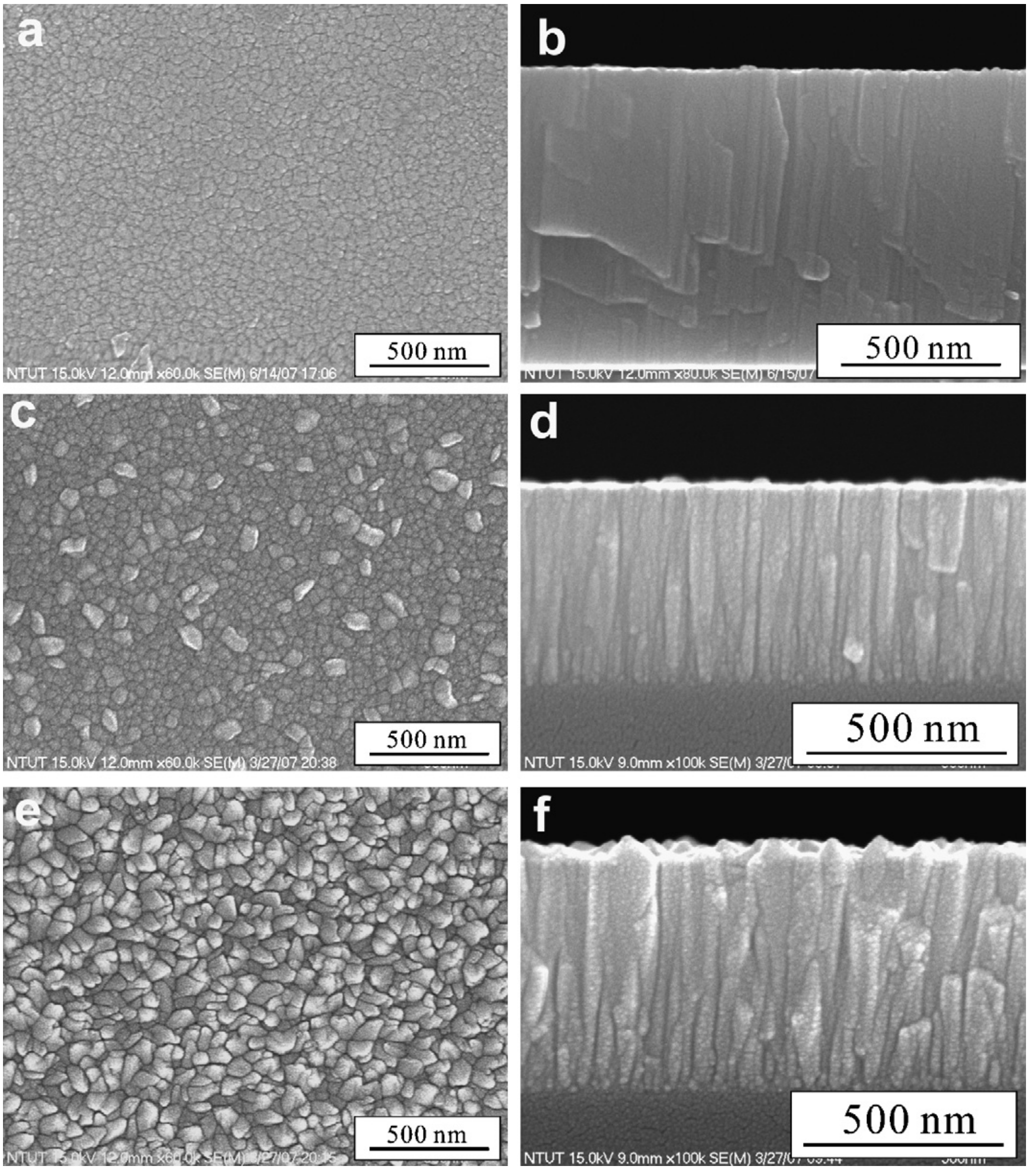

Fig. 2. SEM images of different ZnO seed layers covered on Si substrates: (a) plane-view and (b) cross-sectional view of ZnO-A seed layer, (c) plane-view and (d) cross-sectional view of ZnO-B seed layer, and (e) plane-view and (f) cross-sectional view of ZnO-C seed layer.

75 °C for 1 h. The structure and morphology of as-prepared nanorods were examined using XRD, SEM and HRTEM.

3.2. Effect of seed layers on the crystal structure and morphology of ZnO nanorods

Fig. 3 shows the plane view and cross-sectional view of the nanorod arrays grown on various ZnO seeded substrates. As observed, the morphologies of the nanorods are quite different in terms of the orientation, growth density, and distribution, which are strongly dependent on the properties of the ZnO seed layers. On the top of the ZnO-A seed layers prepared using DC reactive sputtering, ZnO nanorods were not found. For the ZnO-B and ZnO-C seeded substrates deposited via RF magnetron sputtering at power values of 150 and 175 W, respectively, a high density of ZnO nanorods with well-defined hexagonal facets (0 0 2) were grown almost vertically over the entire substrates, as compared with XRD results. Uniformity and alignment are better for the ZnO nanorods grown on the ZnO-C seeded substrate compared with those on ZnO-B seeded substrate having an inclination away from vertical direction. Apparently, prior seeding of the surface by ZnO layer with (0 0 2) preferred orientation leads to nucleation sites on which ZnO nanorod arrays can grow in a highly aligned fashion. Structural analyses using high resolution TEM were also performed on ZnO nanorods grown at ZnO-C seeded substrate. The high resolution TEM image and the corresponding diffraction pattern and lattice-plane spacing (approximately 0.52 nm), as shown in Fig. 4, prove that the nanorods are single crystals with ZnO hexagonal structure. In addition, this shows that the ZnO nanorods were preferentially grown along [0 0 1] direction.

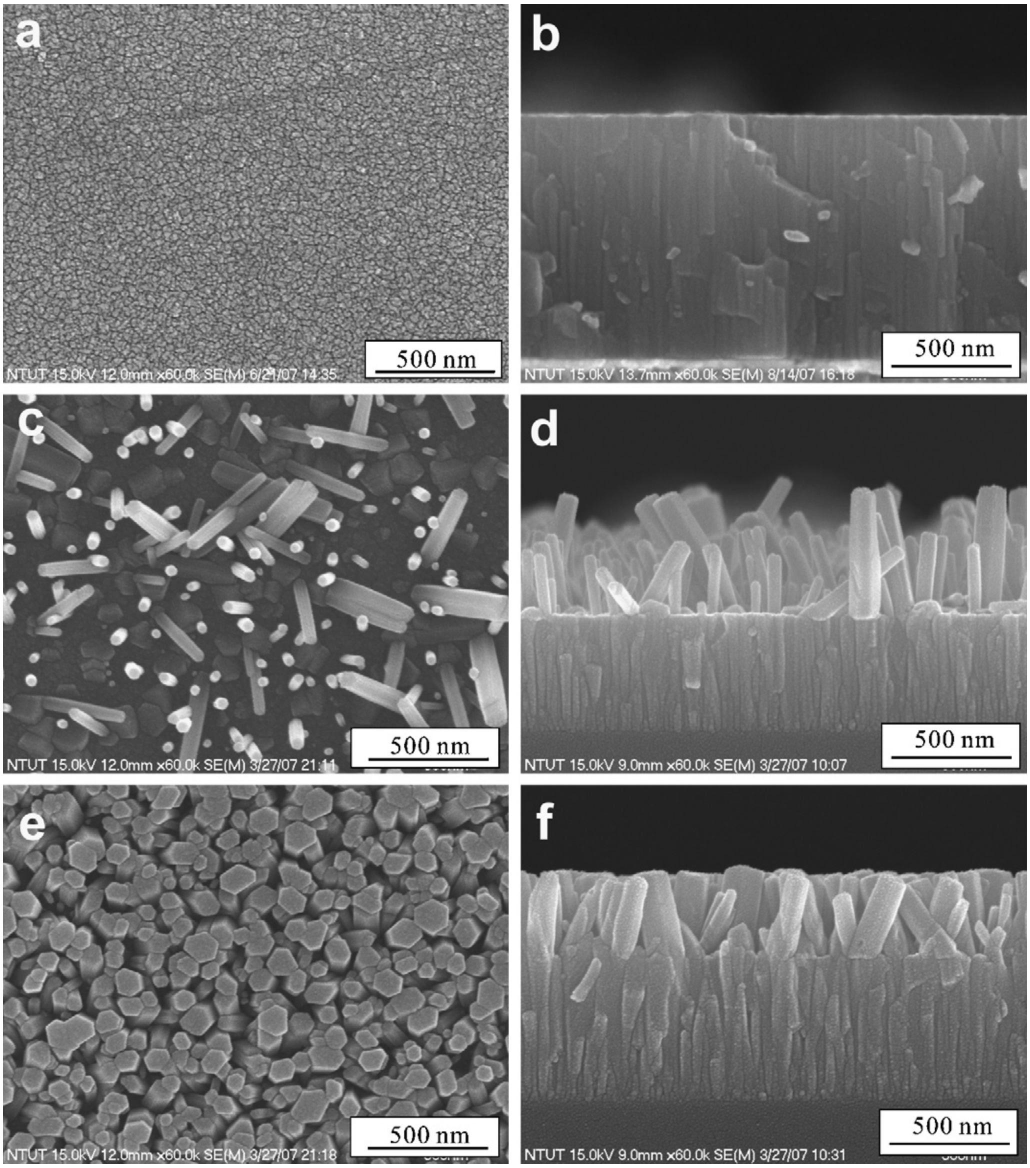

Fig. 3. SEM images of ZnO nanorods grown on Si substrates with different ZnO seed layers: (a) plane-view and (b) cross-sectional view of ZnO nanorod arrays grown on ZnO-A seed layer; (c) plane-view and (d) cross-sectional view of ZnO nanorod arrays grown on ZnO-B seed layer, and (e) plane-view and (f) cross-sectional view of ZnO nanorod arrays grown on ZnO-C seed layer.

Fig. 5 shows the XRD patterns of ZnO nanorod arrays grown on various ZnO seeded substrates. For the nanorods grown on the ZnO-B and ZnO-C seeded substrates, all diffraction peaks can be indexed to the wurtzite structure which confirms the epitaxial growth of ZnO. The crystallinity and growth orientation of the ZnO nanorods are similar to those of underneath ZnO seed layer. A typical hexagonal *c*-axis (0 0 2) was the preferred growth direction. However, XRD pattern scanned on the non-*c*-axis of ZnO-A seeded substrate after solution grown process is similar to the results shown in Fig. 1a, which only shows a weak (1 0 3) peak. The absence of (0 0 2) peak in Fig. 5a confirms that ZnO nanorods with (0 0 2) preferred orientation were not grown on the ZnO-A seeded substrate. In addition, a careful examination of Figs. 2a and 3a and Figs. 2b and 3b, shows that the thicknesses of ZnO layers on the Si substrate before and after the solution growth process are almost the same and no particle or layer was nucleated on the top of ZnO-A layer, which rules out the possibility of ZnO formation with other facets. They clarify that the formation of ZnO nanorods would not prevail on the (1 0 3) ZnO surface. Fig. 6 shows the distribution histograms of the widths of the nanorods obtained from the corresponding SEM micrographs in Fig. 3. The diameter distributions between the ZnO nanorods grown on the ZnO-B and ZnO-C seeded substrates do not have a significant difference. Though the length of the nanorods on the ZnO-C seeded substrate are relatively uniform and around 350 nm, that on ZnO-B seeded substrate are ranging from 320 to 560 nm. Therefore, the underneath pre-sputtered ZnO seed layers play a crucial role for the growth of high-oriented ZnO nanorods.

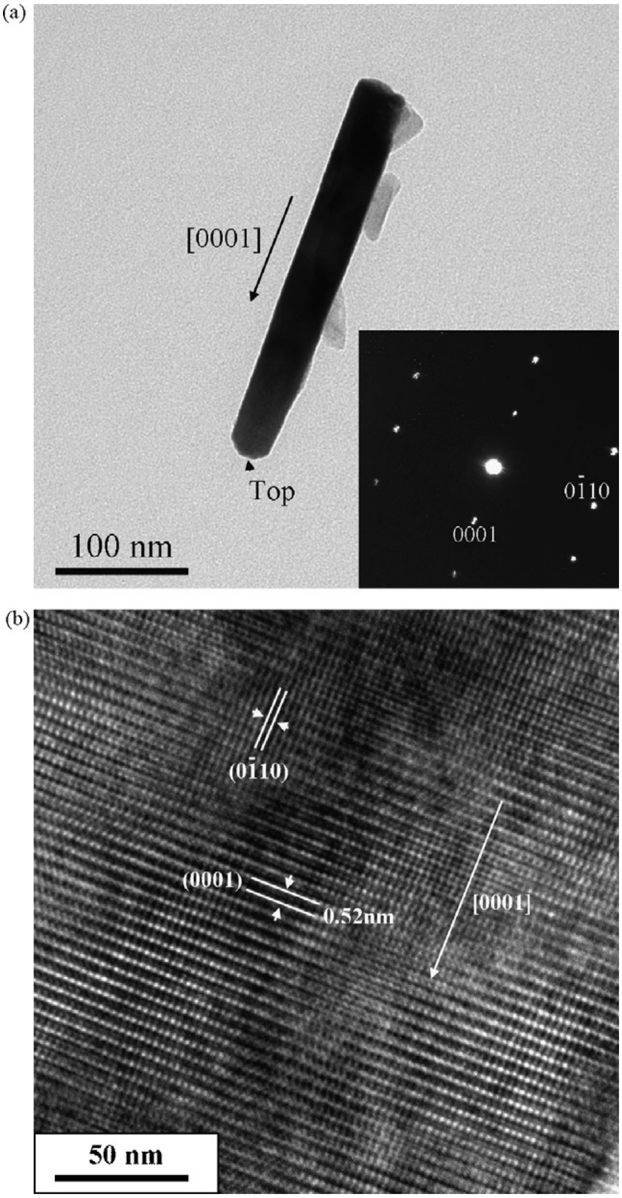

Fig. 4. (a) TEM images with inset SAED pattern of ZnO nanorod grown on ZnO-C seeded substrate and (b) the corresponding high-resolution lattice fringes with calculated and measured interplanar distance of ~0.52 nm.

In the literature, although Vayssieres reported [11] the growth of ZnO nanorods on unmodified substrates from the solution of $Zn(NO_3)_2$ and methenamine, Zhao et al. [21] reported that no nanorods of ZnO were observed on bare glass or ITO slides in solution of $Zn(NO_3)_2$ and NaOH. It is generally agreed that ZnO seeding is required for the aligned ZnO nanorods growth on the substrates. Though heterogeneous nucleation on a foreign surface occurs more easily compared to homogeneous nucleation, the process is difficult for manipulation due to the random and complex nature of nuclei grown on a foreign surface [11,19]. Pre-coating the substrates with seeds of the same material to be grown as nanorods is an easy method to control the oriention and morphology of the nanocrystals [17,23]. In this study, we found that ZnO seed layer with (1 0 3) preferred orientation does not seem to facilitate the formation of ZnO nanorods in the solution grown process. ZnO seeding layer with (0 0 1) direction is essential for the formation of aligned ZnO nanorod arrays. The sequence of reactions

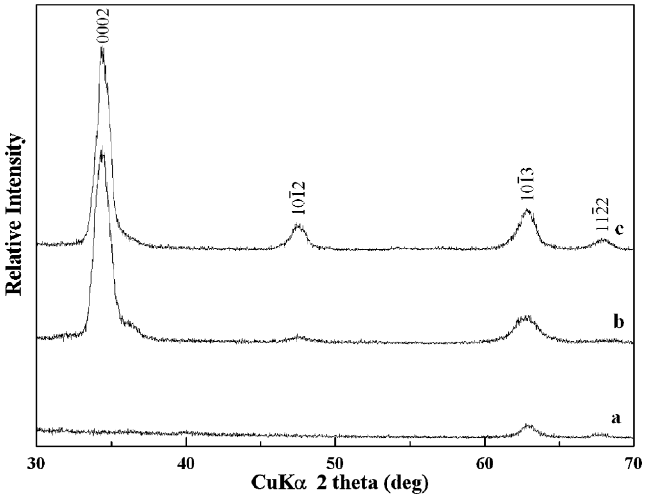

Fig. 5. XRD patterns of ZnO hexagonal nanorod arrays grown on Si substrates with (a) ZnO-A, (b) ZnO-B, and (c) ZnO-C seed layers.

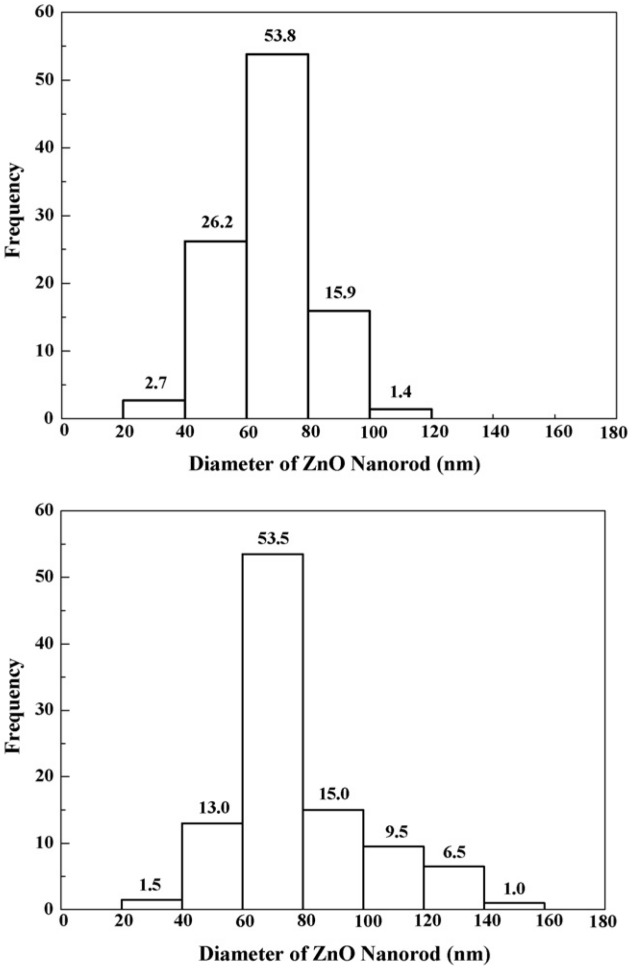

Fig. 6. Diameter distribution of ZnO hexagonal nanorod arrays grown on Si substrates covered with (a) ZnO-B and (b) ZnO-C seed layers.

involved for the ZnO nanorods growth can be expressed as follows [25]:

$$(CH_2)_6N_4 + 6H_2O \rightarrow 6HCHO + 4NH_3$$

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$

$$2OH^- + Zn^{2+} \rightarrow Zn(OH)_2(s) \rightarrow ZnO(s) + H_2O$$

ZnO is a polar crystal, which has a direct moment along (0 0 1) direction. The difference in the heteronucleation behavior of the nanorods on various ZnO seeded substrates may be related to the anisotropy of the ZnO crystal. The polar nature of the (0 0 1) plane can be easily charged positively or negatively by attracting ions of opposite charges (Zn^{2+} and OH^-), which facilitates the growth of ZnO nanorods on the substrates [24]. The crystal planes such as (0 0 1) having higher surface energy possess smaller activation energy for nucleation and faster growth velocity [22]. The (1 0 3) preferred orientation of ZnO-A layer with a smooth surface, prepared using DC reactive sputtering, seems to have a higher energy barrier for nucleation and requires a longer induction time to start the nucleation [9]. Prolonging the reaction time or altering the solution conditions may produce a randomly oriented ZnO nanorod on the ZnO-A seeded substrates.

4. Conclusions

In summary, ZnO nanorod arrays were grown on various ZnO seeded substrates using aqueous solution method. All samples were grown simultaneously in an aqueous solution, containing 0.05 M $Zn(NO_3)_2$ and 0.01 M $C_6H_{12}N_4$, at a constant temperature of 75 °C for 1 h. On the top of the ZnO-A seed layer with (1 0 3) preferred orientation, prepared using DC reactive sputtering, ZnO nanorods were not found. For the ZnO-B and ZnO-C seeded substrates with (0 0 2) preferred orientation deposited via RF magnetron sputtering at a power values of 150 and 175 W, respectively, a high density of ZnO nanorods with well-defined hexagonal facets (0 0 2) were grown almost vertically over the entire substrates. Uniformity and alignment are better for the ZnO nanorods grown on the ZnO-C seeded substrate compared with those on ZnO-B seeded substrate having an inclination away from vertical direction. The crystal planes of (0 0 1) having higher surface energy possess smaller activation energy for nucleation and faster growth velocity, while the (1 0 3) preferred orientation of ZnO layer with a smooth surface seems to have a higher energy barrier for nucleation.

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