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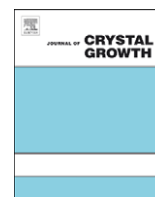


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Controlled *c*-oriented ZnO nanorod arrays and *m*-plane ZnO thin film growth on Si substrate by a hydrothermal method

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ABSTRACT

Oriented ZnO nanorod arrays and ZnO thin films were simultaneously grown on magnetron sputtered ZnO seed layers through a hydrothermal approach without any metal catalyst. The *c*-oriented ZnO nanorod arrays were grown on the unannealed ultrathin ZnO seed layer, while the ZnO thin films with (1 0 0) preferred orientation were grown on the annealed ultrathin ZnO seed layer. Thermodynamically preferred (0 0 2) oriented grain growth will be suppressed by the morphology changes of the ultrathin seed layer while the (1 0 0) orientation will preferentially develop instead. Photoluminescence spectroscopy results show that the UV emission peak shifts slightly to shorter wavelength with increasing the annealing temperature of the ultrathin ZnO seed layer.

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1. Introduction

Zinc oxide (ZnO) has been widely studied because of its unique optical and electrical properties [1]. Recently, zinc oxide nanostructures have received growing attention for their promising applications. Among them, ZnO nanorods have gained increasing interest since they can offer a unique opportunity in fabricating electronic, optoelectronic, electrochemical, electromechanical devices, such as ultraviolet (UV) lasers [2], light-emitting diodes [3], field emission devices [4], solar cells [5], as well as piezoelectric generators [6]. It is also known that the *a*-axis-oriented ZnO films exhibited a higher second harmonic conversion coefficient than those films with the *c*-axis orientation [7] while ZnO thin films are usually deposited with the *c*-axis perpendicular to the substrates due to the lowest surface free energy for the (0 0 2) plane.

Chemical bath deposition (CBD) is one of the useful solution methods for the preparation of compound semiconductors from aqueous solution, with advantages such as low processing temperature, allowing growth upon a variety of substrates and easy adaptation to large area processing at low fabrication cost. In general, the annealing process helped the as deposited catalyst (such as Au [8] and noncatalyst-layer (ZnO seed [9]) to form a uniform crystalline thin layer on the surface of the Si substrate,

which is critical to the oriented growth of aligned ZnO nanorods. There has been a few reports that nonpolar epitaxial growth of ZnO has been previously studied to achieve *a*-plane ZnO on *r*-plane sapphire [10] and *m*-plane ZnO on *m*-plane sapphire [11] using the expensive growth techniques such as laser molecular-beam-epitaxy (MBE) and metal organic vapor phase epitaxy (MOVPE). However, little work has been reported to prepare the dense and adherent *a*-axis oriented ZnO films by the CBD method, not to mention that the change of ZnO nanostructures from the *c*-axis oriented ZnO nanorod arrays to the *a*-axis oriented ZnO nanofilms has been achieved only just by altering the annealing process of as-deposited noncatalyst ZnO seed layer.

In this work, we report a CBD method to prepare ZnO nanostructures with different orientations, evolving from the *c*-axis oriented ZnO nanorods arrays to the *a*-axis oriented ZnO nanofilms, in a controllable way by pre-annealing the seed layer. A pre-annealing-induced growth mechanism is also proposed.

2. Experimental section

Si (1 0 0) wafers were used as substrates. After a standard chemical cleaning, the substrates were loaded into a Jspatter8000 Magnetron Sputtering System. Then, the ZnO ultrathin (approximate 15 nm in thickness) seed-layers were deposited for 5 min at 400 °C using a ceramic ZnO target (99.99% purity). The base pressure was about 2.2×10^{-6} Pa and the working pressure was

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6.4×10^{-1} Pa. After deposition, the samples were immediately annealed at 650 and 750 °C in air ambient for 1 h.

ZnO nanostructures were then grown on the ZnO ultrathin seed-layer by a hydrothermal approach. The seeded substrates were placed in 100 mL of 25 mM equimolar aqueous solution of zinc acetate dehydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2 \text{H}_2\text{O}$) and methenamine ($\text{C}_6\text{H}_{12}\text{N}_4$). The solution was maintained at 90 °C for 2 h using a thermostatically controlled water bath. Finally, the prepared samples were thoroughly washed by deionized water and allowed to dry at room temperature before characterization.

The phase and morphology of the samples were characterized by means of field emission scanning electron microscope (FE-SEM, S-4800, Hitachi), X-ray diffraction (XRD, D8 Advance spectrometer of Bruker AXS with $\text{Cu K}\alpha$ ($\lambda=1.540600 \text{ \AA}$) radiation). The surface morphologies of the seed layers were investigated by atomic force microscopy (AFM, Dimension 3100 V, Veeco). The photoluminescence (PL) measurements were performed at room temperature with a He–Cd laser (325 nm, 15 mW) as the excitation source.

3. Results and discussion

Fig. 1a–c shows the top-view SEM images of the ZnO samples grown on the as deposited, 650 and 750 °C heat treated ZnO seed layers. All the ZnO nanostructures were grown at 90 °C for 2 h. When the ultrathin seed-layer was unannealed, the morphology of the prepared ZnO sample shown in Fig. 1a was vertically well-aligned nanorod arrays with a typical diameter of dozens of nanometers. When the pre-annealing temperature increased to 650 °C, dense film with irregularly shaped crystallites was observed, as shown in Fig. 1b. As the pre-annealing was further increased to 750 °C, as shown in Fig. 1c, the morphology of the CBD-deposited ZnO film was still irregularly shaped crystallites film with smaller crystal size. The results clearly indicate that the morphology changes from nanorod arrays to nano-crystalline films with increasing the annealing temperature of the seed layers.

Fig. 2a–c presents XRD θ – 2θ scans of the samples, corresponding to the SEM images shown in Fig. 1a–c. The patterns fit well with the wurtzite hexagonal phase of the bulk zinc oxide (JCPDS 36-1451). An intense (0 0 2) peak is observed for the ZnO nanorod arrays fabricated on the unannealed ultrathin seed-layer (as shown in Fig. 2a), indicating that the *c*-axis of the nanorods was perpendicular to the substrate surface. The small diffraction peak at 31.77° is also discernable that is indexed to the diffraction peak of ZnO (1 0 0). The other small diffraction peak at 33.03° is attributed to Si substrate which is marked by star. In contrast, a preferred (1 0 0) orientation of ZnO is observed for the samples with the ultrathin seed-layer annealed at 650 °C for 1 h based on the strongest diffraction peak at 31.80° with full width at half maximum (FWHM) of 0.10° as shown in Fig. 2b. The other three weak peaks corresponding to the commonly observed (0 0 2), (1 0 1) and (1 1 0) ZnO diffraction peaks are present at 34.46° , 36.29° and 56.62° , respectively. As the pre-annealing temperature increased to 750 °C, the θ – 2θ pattern in Fig. 2c exhibits the strongest (1 0 0) diffraction peak at 31.77° with FWHM of 0.10° and two weak (0 0 2) and (1 0 1) ZnO diffraction peaks. XRD patterns demonstrate that the preheating temperature of the seed layers directly determines the orientation of the resulting ZnO nanorod arrays and thin films. The transformation from (0 0 2) to (1 0 0) preferred orientation was obtained by increasing the annealing temperature of the ultrathin seed layers. From the future application point of view, the (1 0 0) textured films are beneficial for acousto-optical and piezoelectrical devices [12].

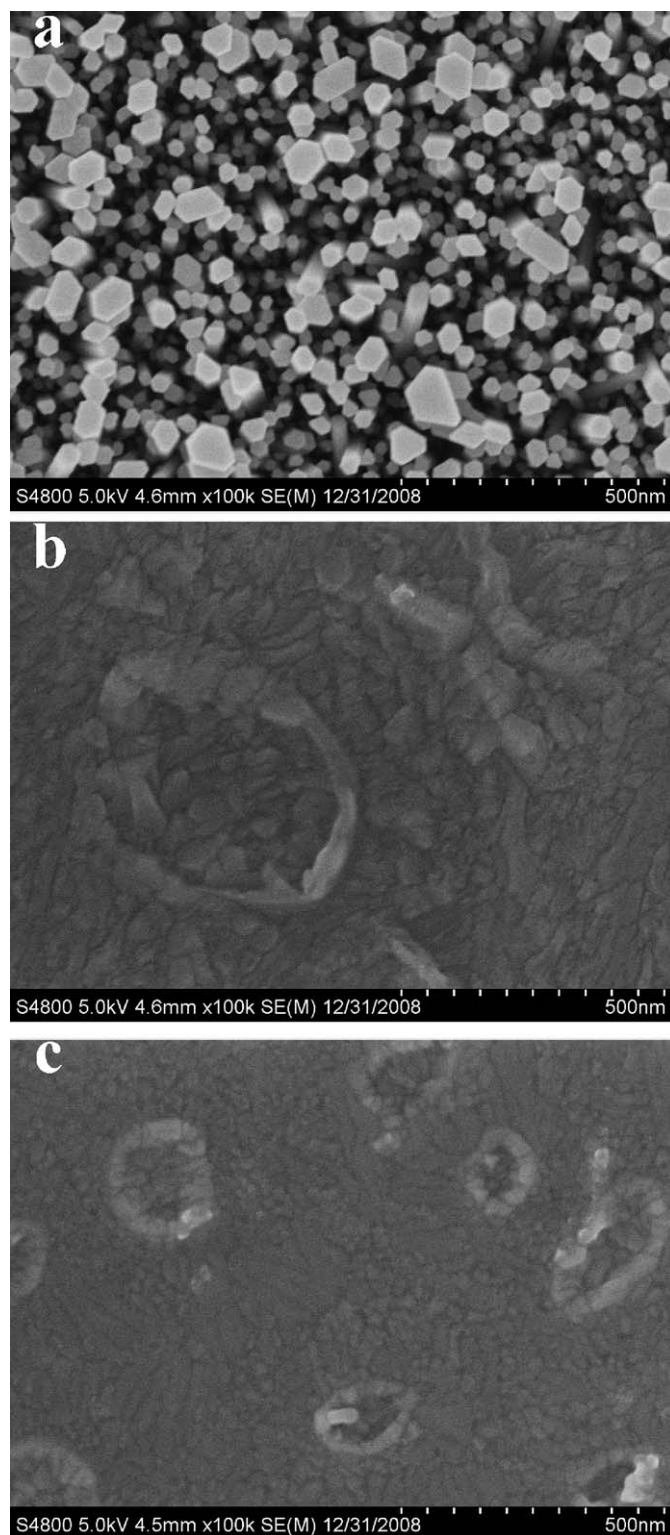


Fig. 1. SEM images of the top view of ZnO nanorod arrays and thin films grown on the ultrathin seed layers annealed at different temperatures: (a) as-deposited; (b) 650 °C; and (c) 750 °C.

As far as we know, the above-mentioned phenomenon has not been reported that preannealing of the seed layers could change subsequent ZnO samples from (0 0 2)-oriented nanorods to (1 0 0)-oriented thin films. As seen in literature, increasing the pre-annealing temperature of the seed layers is believed to be

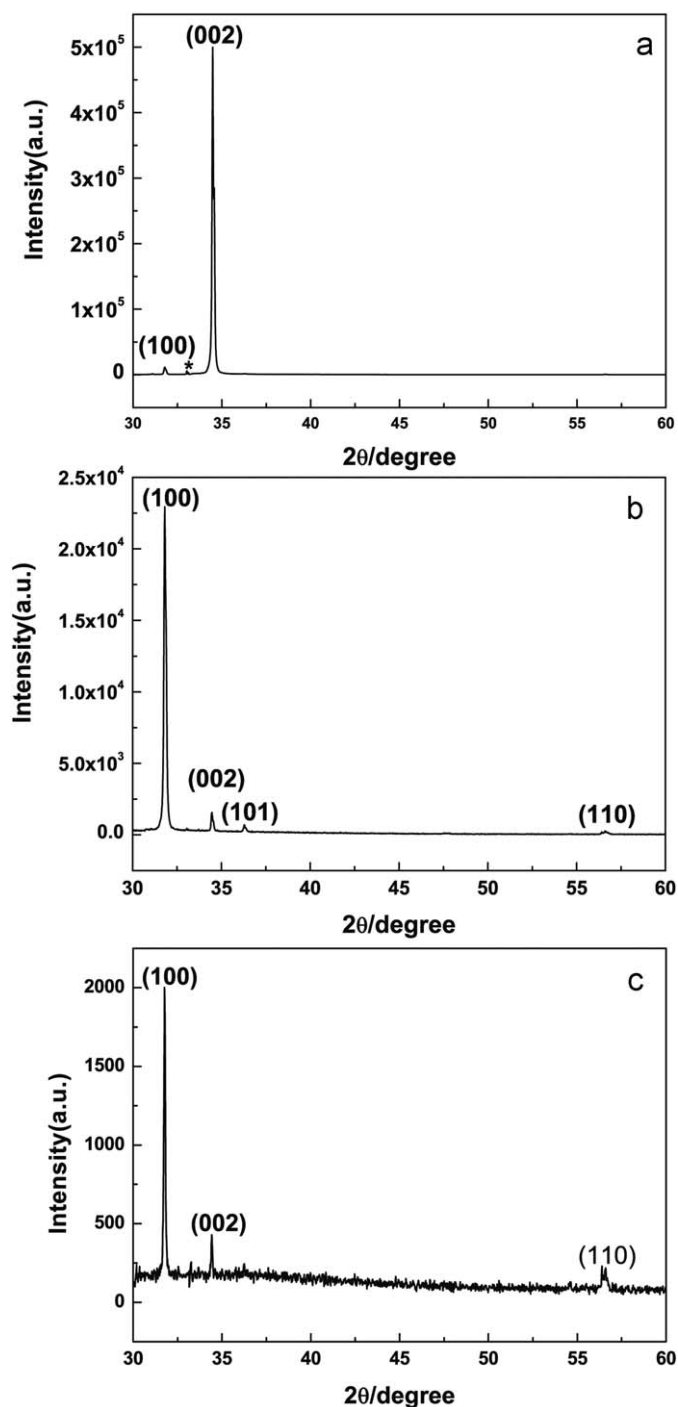


Fig. 2. XRD patterns of ZnO nanostructures grown on the ultrathin seed layers annealed at various temperatures: (a) as-deposited; (b) 650 °C; and (c) 750 °C.

able to improve the growth rate and decrease the density of the corresponding ZnO nanorods [13]. In addition to the annealing temperature of the seed layer, it is speculated that the thickness of the seed layers also plays a key role in the orientation changes. Fig. 3a,b show the XRD patterns of the ZnO nanostructures prepared under the same CBD processing condition except that the sputtering deposition time of the seed layer was extended to 1 h (about 180 nm in thickness). Both sharp and strong ZnO (002) peak presents in the ZnO nanostructures with the seed layer unannealed (shown in Fig. 3a) and the seed layer annealed

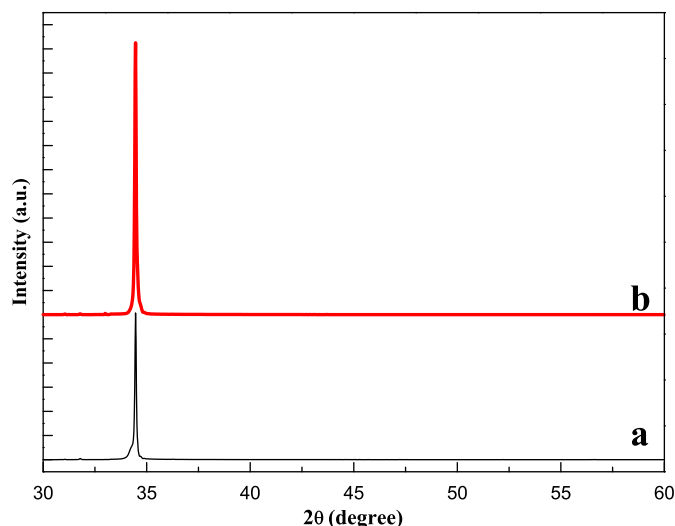


Fig. 3. XRD patterns of ZnO nanostructures grown on the ZnO thick seed layers deposited for 1 h and then annealed at various temperatures: (a) as-deposited and (b) 750 °C.

at 750 °C (shown in Fig. 3b). The intensity of the (002) diffraction peak increases with the increase of the seed layer annealing temperature, which is in good accordance with the study discussed by Liu et al. [8]. It can be revealed that the morphology and the orientation of the subsequent ZnO nanorod arrays could not change whether the thicker ZnO seed layers is pre-annealed or not. Hence it can be concluded that the ultrathin ZnO seed layer is crucial to determine the morphology and orientation transformation.

In order to explore the effect of ultrathin seed-layers on the ZnO nanostructure growth, the morphologies of the sputtered ultrathin ZnO seed-layers annealed at different temperatures were observed by atomic force microscopy (AFM), as shown in Fig. 4a–f. The as-deposited ZnO seed layer is constituted by dense prismatic ZnO seed grains. Annealing treatment of the ultrathin seeded Si substrates at a relatively higher temperature for 1 h would provide enough energy to integrate tiny grains to form a little bit bigger sparse separate ZnO islands, meanwhile oxidizing the uncovered silicon surfaces to form SiO₂ layer. The higher the pre-annealing temperature, the larger the ZnO seed islands and the larger exposed SiO₂ area, as shown in Figs. 4d and 4f. Because the Zn atoms of the ZnO (0001) surface possess positive charge [14] and the SiO₂ surface is slightly negatively charged in aqueous solutions [15], the anionic OH⁻ and zinc cations assemble onto the ZnO-seeded surface and exposed SiO₂ surface separately, then followed by the interactions between adjacent ions as well as atom rearrangement to yield long-range lattice ordering, which is believed to be the possible reason to the growth of nonpolar (100) oriented ZnO nanocrystalline on the post-annealed ultrathin ZnO-seeded layer.

Fig. 5 gives the room-temperature photoluminescence (PL) spectra of the ZnO nanostructures grown on the ultrathin seed layers annealed at different temperatures. The room temperature PL spectra of ZnO (100) and ZnO (002) are quiet similar, in agreement with the other report [16]. No PL from surface state or defect state can be detected and only sharp UV peaks located in the range of 380–382 nm were observed, implying that there are with good crystal quality and low concentration of defects in the ZnO structures. The UV peak position of the ZnO nanostructures is slightly shifted to the shorter wavelength (the inset of Fig. 5),

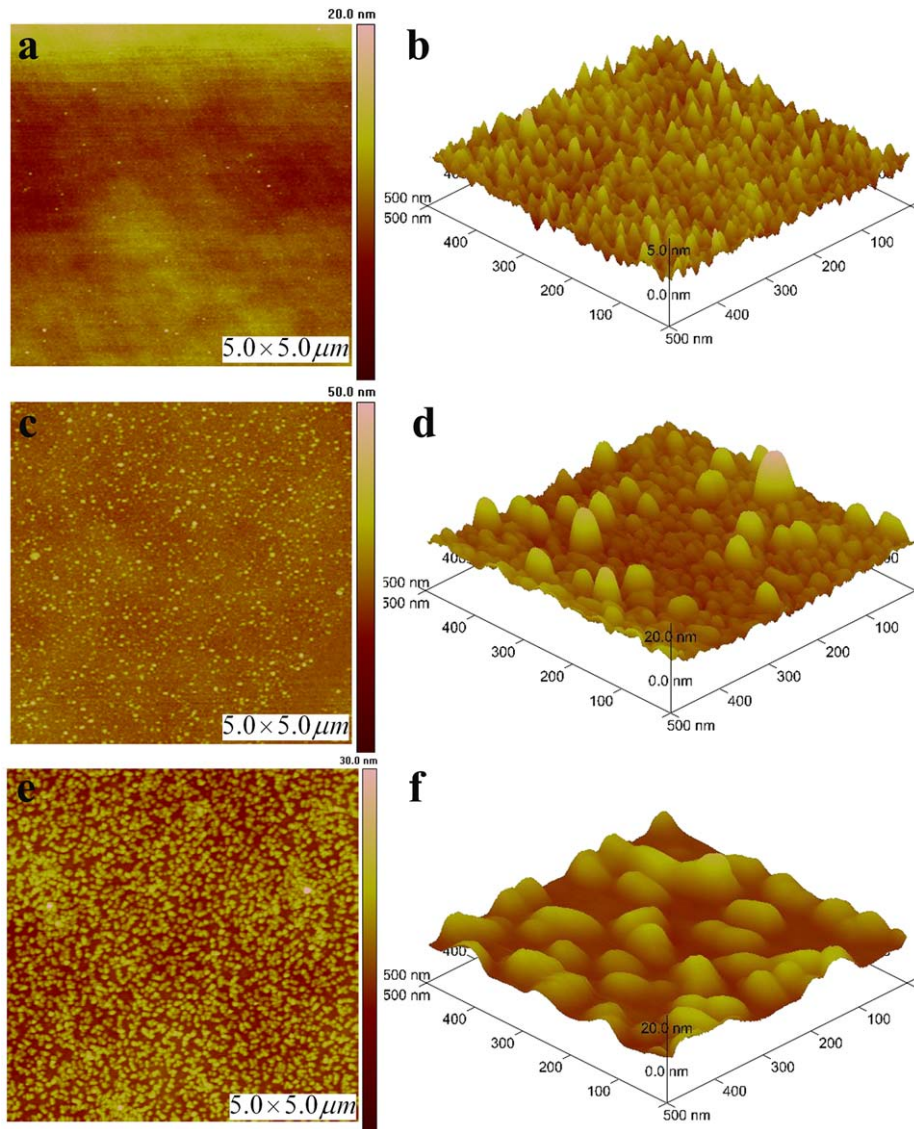


Fig. 4. AFM images of the ultrathin seed layer annealed at various temperatures: (a) and (b) as-deposited; (c) and (d) 650 °C; (e) and (f) 750 °C.

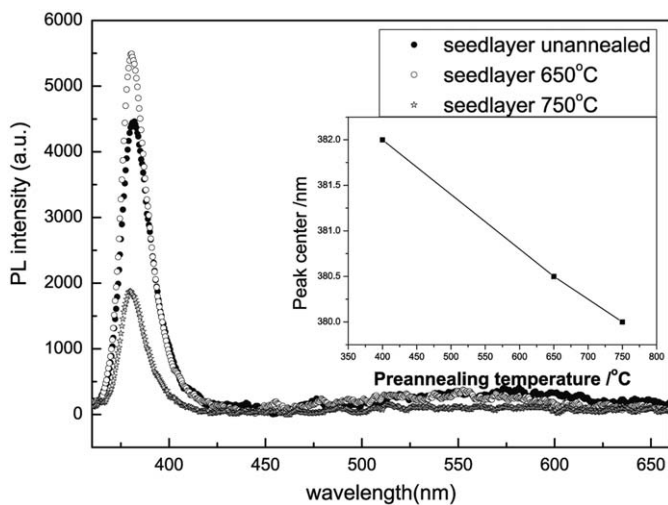


Fig. 5. Room temperature PL spectra of the CBD processed ZnO nanostructures on the ultrathin seed layer annealed at various temperatures: as deposited, 650 and 750 °C.

which may be due to the size effect, as the pre-annealing temperature increased.

4. Conclusions

In this work, the pre-annealing effect of RF magnetron sputtered ZnO seed layers on the preferred orientation, crystallinity and optical properties of the ZnO nanostructures prepared by the hydrothermal method is studied. The ZnO nanorods obtained by the hydrothermal method have a (0 0 2)-preferred orientation on the condition that the ultrathin seeded layer was not annealed and the seeded layer was thicker whether annealed or not. While the ZnO nanocrystalline films have a preferential (1 0 0) orientation when the ultrathin seeded layer were annealed at high temperature. The pre-annealing treatment changed the orientation of the ZnO nanostructures obtained by the hydrothermal method by changing the morphologies of the seeded layers. This approach provides a new strategy for synthesis of (1 0 0) oriented ZnO nanocrystalline films. Room temperature photoluminescence spectra showed that both the obtained (0 0 2) oriented ZnO nanorods and (1 0 0) oriented nanocrystal films have a dominant near

band edge emission and no surface-related and defect related luminescence, indicating that they have good optical properties.

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