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Tunable growth of ZnO nanorods synthesized in aqueous solutions at low temperatures

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Highly arrayed ZnO nanorods were fabricated on the Si substrate buffered with patterned ZnO film (ZnO_f/Si) via wet-chemical process. The growth behavior and morphology of single-crystal ZnO nanorods (ZNs) were investigated in terms of the annealing temperatures of the sputtered ZnO film. We found that the growth morphology of ZnO nanorods is strongly dominated by the grain size of the ZnO film on the Si substrate. The ZnO_f/Si substrate was annealed at above a critical temperature to promote the crystallization of ZnO phase, and high-resolution transmission electron microscopy demonstrated that both ZNs and ZnO_f on Si substrate are coherent. Furthermore, the ZNs seem to nucleate from the concave tip near the grain boundary between two ZnO grains in the ZnO film because of higher surface energy. However, a higher annealing temperature may lead to the formation of a larger ZnO crystal due to the coplanar coalescence behavior of several individual ZnO nanorods. © *2006 American Vacuum Society.* [DOI: 10.1116/1.2163889]

I. INTRODUCTION

One-dimensional ZnO nanocrystals have been extensively studied because of their promising chemical and physical properties[1] and show potential applications in manufacturing electronic and optoelectronic devices.[2,3] In the past, a variety of methods has been employed, including vapor-phase-transport, metal-organic chemical-vapor deposition to grow arrayed nanorods and nanowires of ZnO from aqueous solutions. Recently, many wet-chemical approaches have been developed to prepare oriented arrays of ZnO nanorods on polycrystalline (or single crystalline) substrates from aqueous solutions. Choy *et al.* reported that the buffer layer of dip-coated ZnO nanoparticles can effectively reduce the mismatch between the Si substrate and the ZnO nanorods.[4] Our previous report also suggested that on a Si wafer coated with a ZnO film, well-aligned ZnO nanorods (ZNs) with different aspect ratio can be grown along the [0002] direction on the Si substrate coated with ZnO film (ZnO_f/Si substrate).[5] All the observations reveal that the undercoating ZnO film plays a very important role in the development of ZNs. However, no systematical studies have been performed up to now. Therefore, in this work, we investigate the effect of annealing treatment of the undercoating ZnO film on the growth behavior of ZNs. Furthermore, it was found that the ZNs can be selectively grown on a patterned ZnO film which can serve as seeds to modify the morphology of ZNs by controlling the annealing condition of the coated ZnO film on any substrates.

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II. EXPERIMENTAL PROCEDURE

Methenamine ($C_6H_{12}N_4$) and zinc nitrate hexahydrate $[Zn(NO_3)_2 \cdot 6H_2O]$ were used for preparing the solution to grow ZnO nanorods (ZNs).[6] Following our previous report, the Si substrates were buffered with ZnO film by rf magnetron sputtering.[7] Subsequently, the ZnO film/Si substrates (designated as ZnO_f/Si) were annealed at 400–800 °C in N_2 atmosphere to change the crystallinity and morphology of the buffered ZnO films. After that, the annealed ZnO_f/Si substrates were then placed in the aqueous solution of 0.01*M* at 75 °C for 10 h to grow the ZnO nanorods. After growth, the substrates were removed from the aqueous solutions, rinsed with distilled water, and dried at room temperature overnight. The structural characteristics of the ZnO nanorods were analyzed by scanning electron microscopy/energy dispersive x-ray spectroscopy (SEM/EDS, JEOL-6500F) and transmission electron microscopy (TEM) (Philips Tecnai 20). The crystal structure was determined using x-ray diffraction (XRD) with Cu $K\alpha$ radiation. Photoluminescence of the ZnO nanorods was performed by the excitation from a 325 nm He–Cd laser at room temperature.

III. RESULTS AND DISCUSSIONS

Figure 1 shows the atomic force microscopy (AFM) images of the ZnO film sputtered on Si substrate (ZnO_f/Si) at different annealing temperatures. It was found that the grain size of the ZnO film on Si substrates becomes larger and the surface morphology becomes rough with the increase of annealing temperature. Furthermore, it can be observed in Fig. 1(b) that many abnormally large ZnO grains were grown on the ZnO_f/Si substrate annealed at 800 °C. Furthermore, according to our previous study, it was found that the diameter

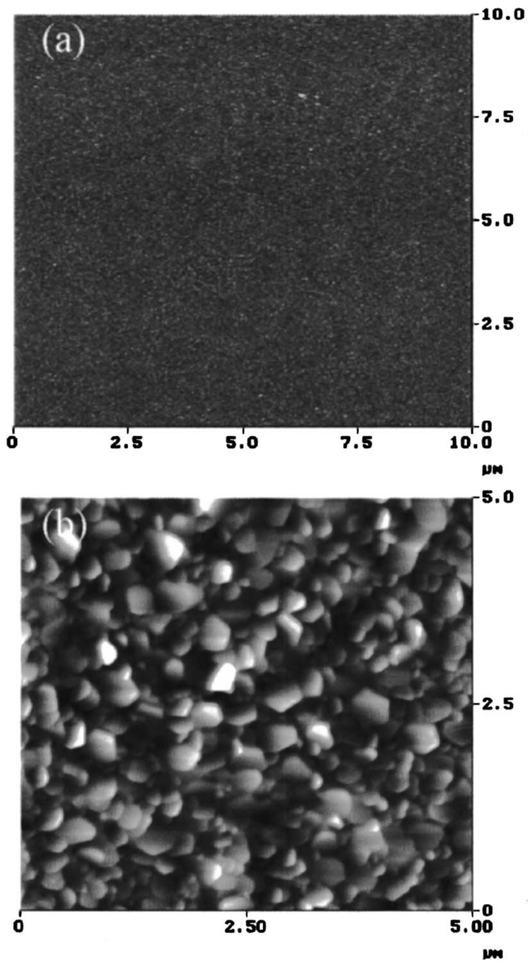

FIG. 1. AFM images of (a) as-grown ZnO films and (b) annealed ZnO film at 800 °C.

of ZnO nanorods was affected by the concentrations of the aqueous solution. Therefore, the same concentration of the precursors $(0.01M)$ was used in this work to avoid the effect of solution concentration. Figure 2 shows the SEM images of the ZNs grown on the patterned ZnO_f/Si annealed at different temperatures, where the patterned ZnO film on Si substrate was fabricated by the photolithography and etching process. As the patterned ZnO_f/Si substrate was placed into the aqueous solution to grow ZNs, well-aligned ZNs are grown on the designed substrate, as shown in Fig. 2(a), and this demonstrates the selected growth behavior of the ZNs. Figure 2(b) shows the surface images of large-scale arrayed ZnO nanorods grown on the patterned ZnO_f/Si at room temperature, and the ZnO nanorods have a well-defined hexagonal plane with a homogeneous diameter. Although the ZnO_f/Si substrate was patterned, nucleation of the nanorods was not correlated with the substrate patterning and subsequent growth of the ZnO grains was also unaffected by patterning. However, as the patterned substrates were first annealed at 600 and 800 °C, prior to the growth of the ZNs in the solution at 75 °C, we found that the morphology of the ZNs was markedly changed, as shown in Figs. 2(c) and 2(d), especially for the ZnO_f/Si annealed at 800 °C. Furthermore,

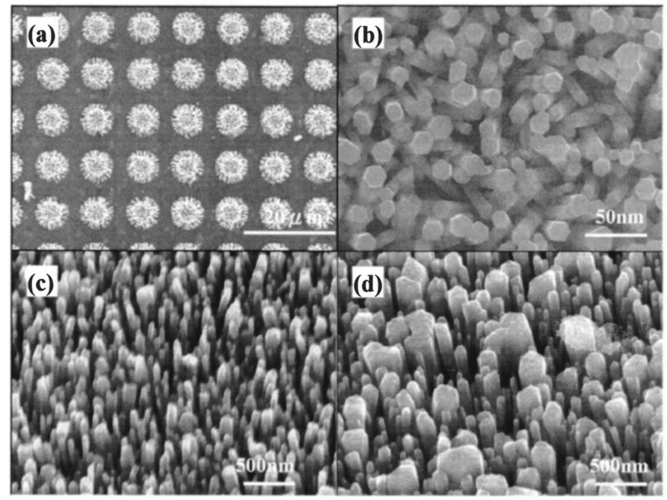

FIG. 2. SEM images of the ZnO nanorods (a) grown on the patterned ZnO_f/Si, (b) grown at room temperature, and grown on the annealed ZnO_f/Si at (c) 600 °C and (d) 800 °C.

the dimension of ZNs increases with increasing annealing temperature. The average dimension of the ZNs is 20 and 300 nm in diameter for the ZnO_f/Si at room temperature and annealed at 800 °C, respectively. When compared with the AFM images of ZnO film on Si substrate shown in Fig. 1, this seems to imply that the growth behavior of the ZNs is correlated with the grain size of the ZnO film sputtered on Si substrate, as illustrated in Fig. 3. Furthermore, there exists a critical temperature around 400 °C, and above that, the ZNs are rapidly grown and become larger in diameter.

Figure 4(a) shows the TEM bright-field (BF) image of the aligned ZNs grown on the annealed ZnO_f/Si substrate at 600 °C. It was observed that most of the ZNs were grown along the direction perpendicular to the ZnO_f/Si substrate. The TEM dark-field image marked with arrows in the Fig. 4(b) reveals that there exists a close relationship between ZNs and ZnO film. Both ZNs and ZnO_f on Si substrate were grown along the same direction of [0002] and are coherent, as demonstrated by the selected-area electron diffraction

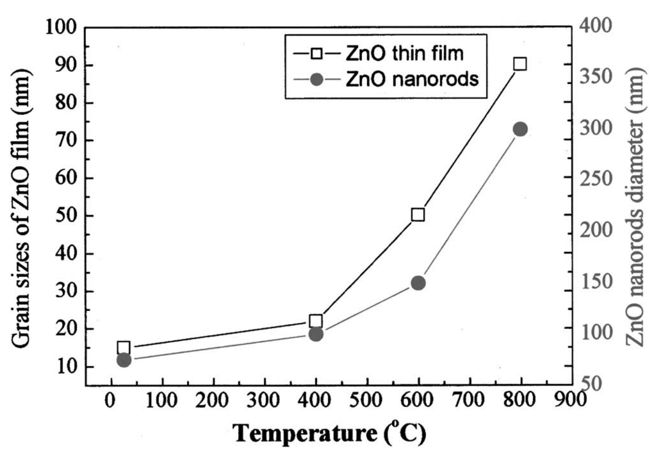

FIG. 3. Both ZN diameter and ZnO_f grain size as functions of annealing temperature.

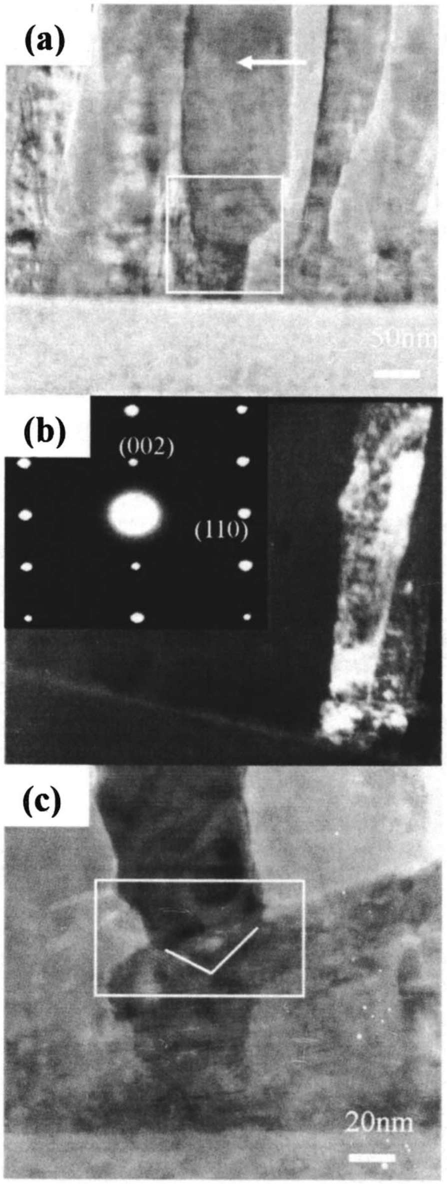

FIG. 4. TEM (a) bright-field and (b) dark-field images of the aligned ZNs grown on ZnO_f/Si substrate annealed at 600 °C. A corresponding diffraction pattern is shown in the inset of (b) for the selected single nanorod. (c) A high-resolution TEM image of (a) showing the interface between ZNs and ZnO_f.

(SAED) pattern [inset of Fig. 4(b)]. In addition, as one observes the interface between ZNs and ZnO_f/Si shown in Fig. 4(c), the high-resolution TEM (HRTEM) image [magnified from the marked area in Fig. 4(a)] reveals that both the ZNs and ZnO films have identical parallel lattice fringes. This indicates that the ZNs seem to nucleate from the concave tip near the grain boundary (marked as lines) between two ZnO grains in ZnO films because it (near the concave tip) has a higher surface energy. A detailed discussion can be referred to Ref. 5.

As the ZnO_f/Si substrate was annealed at a higher temperature of 800 °C, a low-magnification TEM image of the ZNs was shown in Fig. 5(a). The HRTEM image of the ZNs marked with the box in Fig. 5(a) was further illustrated in

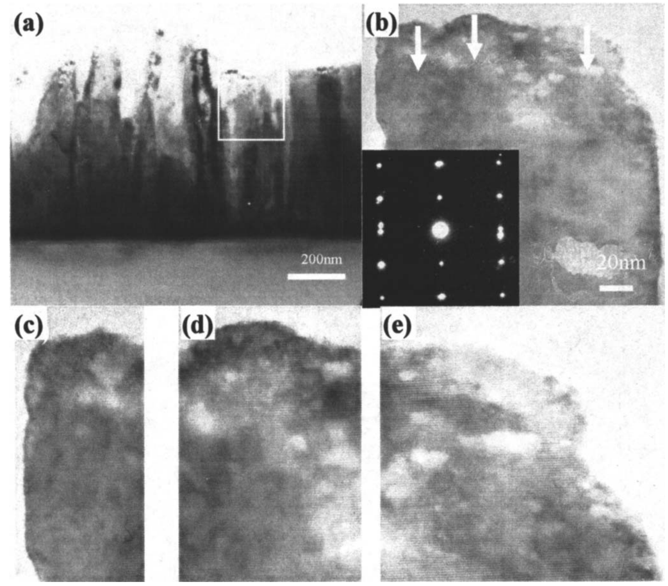

FIG. 5. (a) Showing the low-magnification TEM images of ZnO nanorods grown on the annealed ZnO_f/Si at 800 °C. (b) HRTEM images of the ZnO nanorods marked in the frame of (a) along with split diffraction pattern in the inset. HRTEM image of the (c) left, (d) middle, and (e) right side of the larger nanorod, showing that the larger ZnO nanorod seems to be composed of three ZNs.

Fig. 5(b) where some nanorods are merged together to form a larger ZN along similar growth direction [0002].[8] The selected-area diffraction pattern (SADP) [shown in the inset of Fig. 5(b)] reveals that the diffraction spots were split with several different angles. This suggests that the larger ZNs are not perfectly single crystalline and are consist of three ZNs, as illustrated in Figs. 5(c)–5(e), with a slight misalignment between the nanorods. Therefore, the growth behavior of the larger ZnO nanorods can be considered from the direct combination of a small number of individual nanorods having a similar orientation.[9]

IV. CONCLUSIONS

We demonstrated that the growth of patterned ZnO nanorods can be controlled by changing the annealing conditions of the ZnO_f/Si substrates. When the ZnO_f/Si substrate was annealed above a critical temperature to promote the crystallization of ZnO phase, both ZNs and ZnO_f on Si substrate were found to become crystallographically matched. In this work, it reveals that the ZNs seem to preferentially nucleate from the cup tip near the grain boundary between two ZnO grains in the ZnO film. However, a higher annealing temperature may lead to the formation of a larger ZnO crystal due to coplanar coalescence behavior of several individual ZnO nanorods.

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[1]D. P. Norton, Y. W. Heo, M. P. Ivill, K. Ip, S. J. Pearton, M. F. Chisholm, and T. Steiner, Mater. Today **7**, 34 (2004).
[2]M. H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, and P. Yang, Science **292**, 1897 (2001).
[3]W. I. Park, G.-C. Yi, M. Kim, and S. J. Pennycook, Adv. Mater. (Weinheim, Ger.) **15**, 526 (2003).
[4]J. H. Choy, E. S. Jang, J. H. Won, J. H. Chung, D. J. Jang, and Y. W. Kim, Adv. Mater. (Weinheim, Ger.) **15**, 1911 (2003).
[5]S. C. Liou, C. S. Hsiao, and S. Y. Chen, J. Cryst. Growth **274**, 438 (2005).
[6]L. Vayssieres and K. Keis, J. Phys. Chem. B **105**, 3350 (2001).
[7]C. C. Lin, C. S. Hsiao, S. Y. Chen, and S. Y. Cheng, J. Electrochem. Soc. **151**, G285 (2004).
[8]B. Liu and H. C. Zeng, J. Am. Chem. Soc. **125**, 4430 (2003).
[9]J. T. Sampanthar and H. C. Zeng, J. Am. Chem. Soc. **124**, 6668 (2002).