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Synthesis and physical characteristics of AlO_x-coated ZnO nanorod arrays grown in aqueous solution at low temperatures

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Abstract

AlO_x–ZnO core–shell nanorods arrays have been successfully synthesized by soaking the ZnO nanorods in the sol–gel solution of $Al(NO_3)_3$ and NH_4OH at room temperature. It was found that both crystal growth and morphology of the AlO_x–ZnO core–shell nanorods are strongly influenced by the solution pH value. SEM image shows that the AlO_x–ZnO core–shell nanorods can be perpendicularly grown on the ZnO_f/Si substrate under the solution only with a pH value of 6–7. High-resolution TEM observation demonstrates that the structure of the AlO_x layer is amorphous and the ZnO nanorod core remains single crystal. After annealed at 400 °C in N_2 atmosphere, a strong photoluminescence peak corresponding to blue emission (~450 nm) was detected from the AlO_x–ZnO core–shell nanorods that may result from the induced defects due to interaction between AlO_x shell and ZnO nanorods.

Keywords: D. Blue luminescence

1. Introduction

ZnO has been recognized as one of the promising nanomaterials in optoelectronic device applications, e.g., gas sensors [1], transparent conductors in thin-film transistors [2], optical waveguides [3], and solar cells [4]. Furthermore, it was recognized that doping can also enhance the conductivity of 1D nanowires. Aluminum doped zinc oxide (AZO) films have been widely studied because they exhibit high transparency and low resistivity that are important for transparent conductor. Recently, Al-doped ZnO nanowires grown by vapor–solid–liquid method have been studied. Hung and co-workers [5] reported that the introduction of Al led to the degraded optical properties of the ZnO nanowires but the threshold emission field could be significantly decreased from 16 to 10 V/mm. However, so far, little study has been made to investigate the synthesis and physical properties of ZnO-based core–shell nanostructures. Hwang et al. proposed a process to develop Al_2O_3 nanotubes that were prepared by first depositing Al_2O_3 on ZnO nanowires by atomic-layer deposition (ALD) and then wet-etching the ZnO core nanowires in the ZnO/Al_2O_3 core/shell nanofibers [6]. However, the process is very complex and hard to be reproduced. On the other hand, in the past few years, it has been demonstrated that wet-chemical deposition shows potential for the fabrication of ZnO nanorods due to its simply, low-cost and low-temperature process. Therefore, in this work, a wet-chemical process was developed to grow AlO_x-coated ZnO nanorods on ZnO_f/Si substrate. The self-catalyzed growth of AlO_x–ZnO nanorods on ZnO_f/Si substrate was reported in this study. The physical and optical properties of the AlO_x–ZnO nanorods will be also investigated.

2. Experimental details

The ZnO nanorods were grown on Si substrates coated with ZnO film following our previous report [7]. Following sol–gel process proposed by Hulteen and Martin [8], 5 M ammonia was added to an aqueous alumina nitrate solution (0.4 M) at room temperature. The final pH of the solution was kept about 8.5. The hydrated precipitate

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so formed was centrifugally separated, washed several times with distilled water and peptized with nitric acid to obtain a translucent, homogeneous and stable sol. Subsequently, the grown ZnO nanorods were immersed in the precursor sol of Al^{3+} for 10 s and then removed out for drying in the oven at 105 °C for 24 h.

X-ray diffractometer (M18XHF, MAC Science, Tokyo, Japan) was used to examine the crystalline phase of the synthesized AlO_x–ZnO nanorods. The growth morphology of the AlO_x–ZnO nanorods was examined by scanning electron microscopy (SEM; Hitachi model S4000). Microstructure observation was performed by transmission electron microscopy (TEM) with a Philips Tecnai CM200 instrument, operated at 200 keV. Photoluminescence (PL) was excited by the 325 nm wavelength of an LiF light.

3. Results and discussions

Fig. 1(a) shows SEM images of arrayed ZnO nanorods grown vertically on the substrate. As the ZnO nanorods were immersed in the Al^{3+}-peptized solution with pH 5–6, it was found that the ZnO nanorods were collapsed and transformed into nanoparticles as shown in Fig. 1(b). However, as the pH value of the solution was adjusted between 6.0 and 8.0, Fig. 1(c) shows that the nanorods remained unchanged and highly oriented. This result suggests that the microstructure of original ZnO nanorods was strongly affected by the pH values of the Al^{3+}-peptized solution.

To understand how the microstructure of the as-grown ZnO nanorods was affected by the Al^{3+}-peptized solution, X-ray diffractometry (XRD) and Fourier transform infrared spectroscopy (FTIR) of the samples were analyzed. Fig. 2 shows the XRD spectra of the ZnO nanorods grown in various pH solutions. It was observed that the ZnO phase disappeared in the Al^{3+}-peptized solution with pH 4–6. This may be attributed to the fact that the ZnO nanorods were easily etched by nitric acid. However, as the ZnO nanorods were immersed in the Al^{3+}-peptized solution in the range of pH 6–9, a single strong ZnO (0 0 2) peak at $2\theta = 34.4^\circ$ was detected, indicating that the crystalline phase of ZnO nanorods was remarkably influenced by the peptized solution.

As mentioned above, the pH value in the peptized solution plays a key role in the morphology and phase development of the ZnO nanorods. FTIR was further used to analyze the peptized solution. As shown in Fig. 3, the bands at 1390 cm^{-1} were attributed to the NO_3^- ions and the bands at 1042 cm^{-1} were assigned to the NH_3 wagging modes. The bands between 600 and 800 cm^{-1} may be contributed from the alumina complex. For a peptized solution in an acidic condition (pH value below 6), a strong NO_3^- band was observed, indicating the formation of NH_4NO_3 compound. Therefore, when the ZnO nanorods were immersed in the acidic solution, it would be etched under this circumstance. In addition, a peak of alumina complex was observed in the FTIR curve ranging between 600 and 800 cm^{-1}. It was believed that a ligand-exchange reaction between the surface site Al–OH and the dissociated form (A^-) of humic acid could take place, as illustrated here [9].

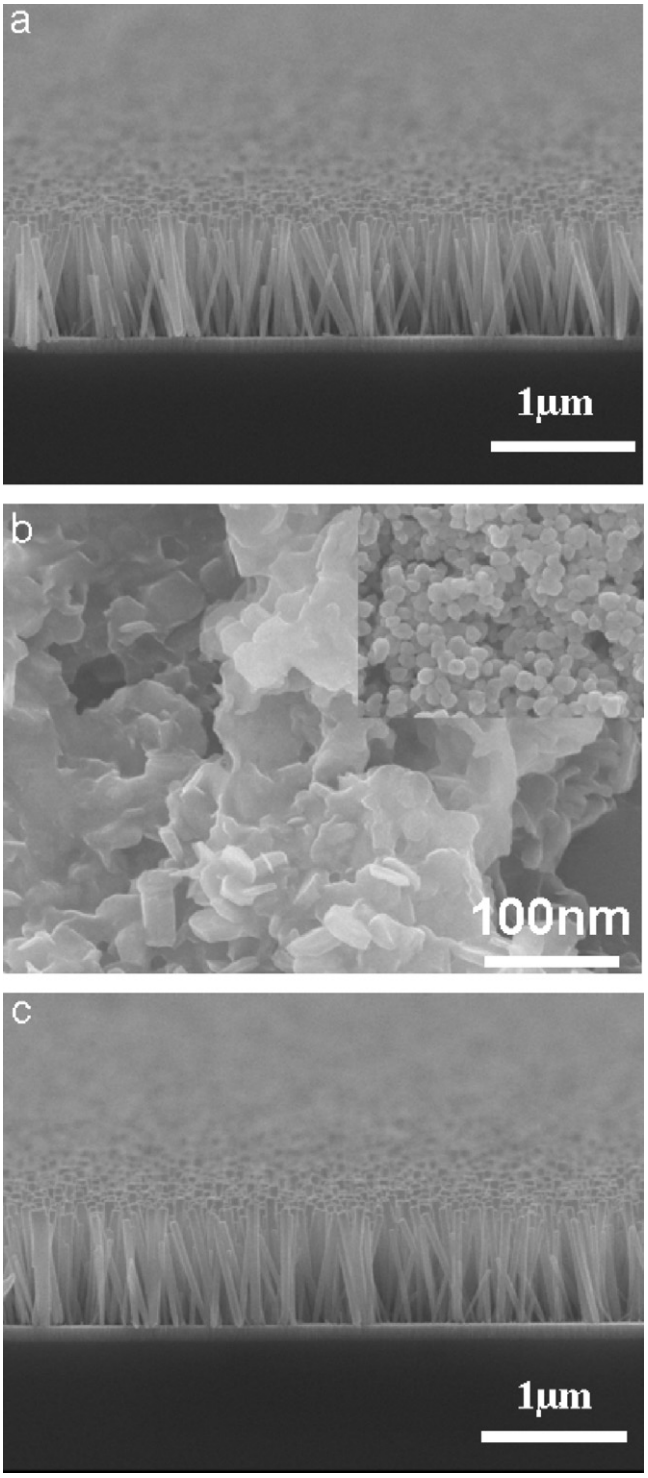

Fig. 1. SEM images of (a) the as-grown ZnO nanorods and those immersed in the peptized solution at pH (b) 4–5 and (c) 6–7 values.

$$Al{-}OH_2^+ \cdots A^- + H^+ + NO_3^-$$

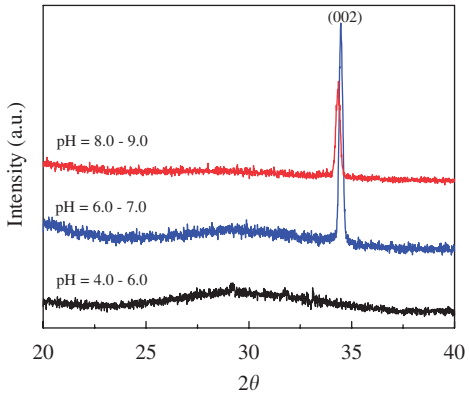

Fig. 2. X-ray diffraction patterns of ZnO nanorods immersed in the various pH-value solutions.

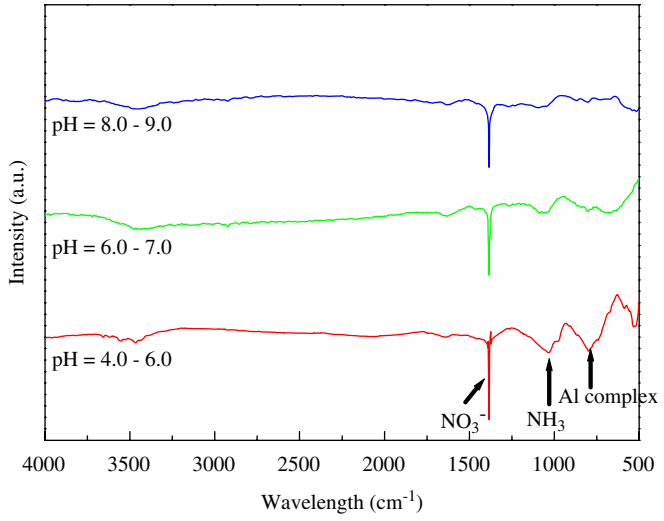

Fig. 3. Fourier transform infrared spectroscopy (FTIR) of the Al^{3+}-peptized solution as a function of pH value.

However, for a solution with pH 6–9, the following ligand-exchange reaction would become dominant:

$$Al-OH + A^- = Al-A + OH^-$$

Therefore, no obvious peak in the range of 600–800 cm^{-1} was identified from the FTIR curve. This may reveal that it is possible for the interaction between Al-peptized solution and ZnO nanorods in this condition.

The high-resolution TEM (HRTEM) images in Fig. 4 show microstructure of the hetrostructured core (ZnO)–shell (Al compound) nanorods. The diameter of the core (ZnO nanorods) and the shell (AlO_x) thin layer was estimated about 20 and 7 nm, respectively. The {0 0 0 2} lattice fringe of the ZnO core nanorod was parallel to the basal plane but no lattice fringe can be identified in AlO_x shell layer, indicating that the shell layer was amorphous. The EDS analysis in mark-1 region presents a strong ZnO signal but no Al element. In contrast, in mark-2 region, the ZnO signal becomes weak but Al element can be detectable compared to those of mark-1. The TEM image suggests

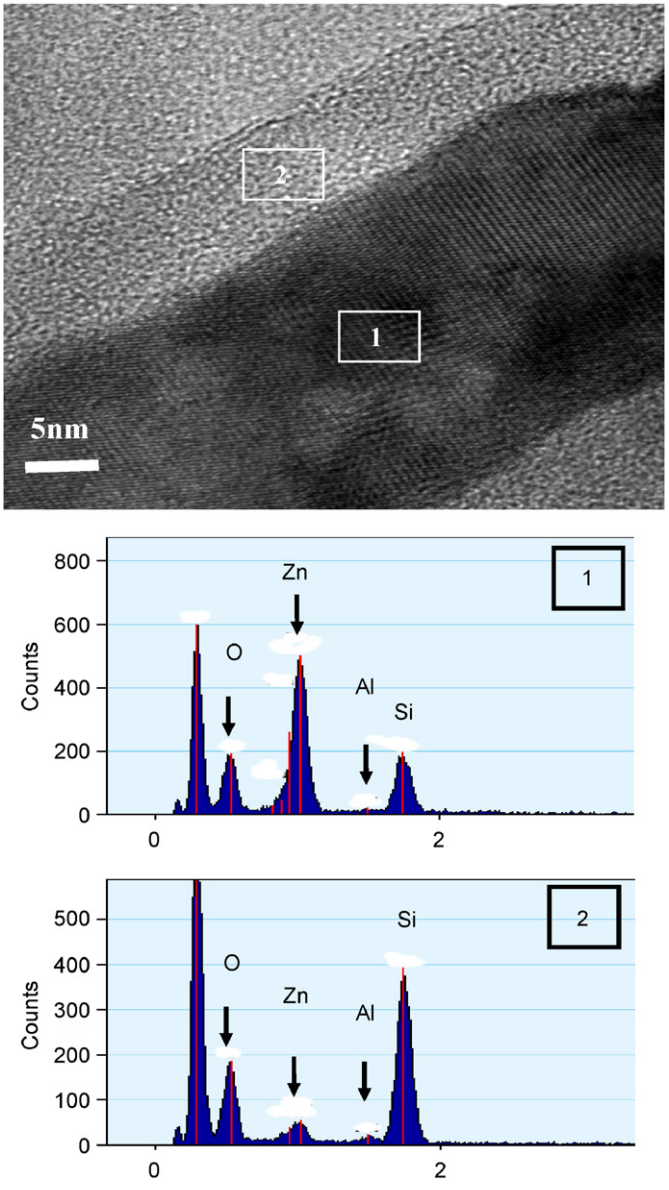

Fig. 4. High-resolution TEM (HRTEM) image of AlO_x–ZnO core–shell structure and its EDS analysis.

that the ZnO nanorods are not damaged and the AlO_x layer on ZnO nanorods has been formed.

Fig. 5 shows the room temperature PL spectra of the ZnO–AlO_x core–shell nanorods that were rapid thermally annealed at 400 °C for 20 min in N_2 atmosphere. A strong PL peak corresponding to blue emission (~450 nm) was observed that was different from the as-grown ZnO nanorods peaked at around 378–382 nm. This may suggest that the blue emission may result from the interaction between AlO_x shell and ZnO nanorods and thus point defect related to this peak was induced. Therefore, a strong blue emission instead of intrinsic ultraviolet emission was detected [10]. The detailed discussion for blue emission of the AlO_x-coated ZnO nanorods is under investigation and will be published in the future work.

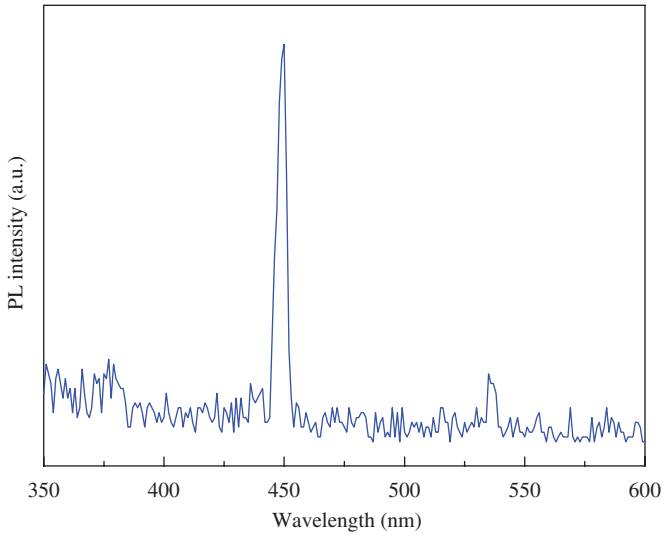

Fig. 5. PL spectra of the AlO_x–ZnO core–shell nanorods annealed at 400 °C in N_2 atmosphere.

4. Summary

A low-temperature synthetic route was developed to grow oriented AlO_x–ZnO core–shell nanorods by controlling the pH values of the peptized solution and annealing temperature. SEM image shows that the AlO_x–ZnO core–shell nanorods are perpendicularly grown on the ZnO_f/Si substrate when the solution was only controlled at around pH 6–7. HRTEM observation demonstrates that the structure of the AlO_x layer was amorphous and the ZnO nanorod core remains single crystal. After annealed at 400 °C in N_2 atmosphere, a strong blue emission peaked at around 450 nm was detected from the AlO_x–ZnO core–-shell nanorods.

Acknowledgment

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