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Growth and optical properties of ZnO nanorods prepared through hydrothermal growth followed by chemical vapor deposition

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ABSTRACT

We report on the synthesis of high-quality ZnO nanorods by combining hydrothermal growth (HG) and chemical vapor deposition (CVD) processes. Vertically aligned and closely packed ZnO nanorods were grown by HG on a sputtered ZnO seed layer on a SiO_2/Si (0 0 1) substrate. The top surface of the HG-prepared ZnO nanorods showed very flat surfaces compared with that of the sputtered ZnO seed layer. Therefore, the HG-prepared ZnO nanorods were used as a new alternative seed material for the CVD growth of the ZnO nanorods. Vertical ZnO nanorods were grown by CVD on both the new HG-prepared nanorod seed material and the sputtered ZnO seed layer. The CVD-prepared ZnO nanorods on new HG-prepared nanorod seed material showed better crystalline quality and superior optical properties than the CVD-prepared ZnO nanorods on sputtered seed layer. The former showed negligible deep-level emissions at room temperature photoluminescence measurements. The intensity ratio of near-band-edge emissions to deep-level emissions from the former was about 910, but that from the latter was about 151. This implies that the HG-prepared ZnO nanorods can be used as a promising new seed material for nanostructure synthesis.

1. Introduction

Zinc oxide-based nanostructures have received increasing attention because of their potential applicability as emitters and sensors [1,2]. Catalyst-assisted and catalyst-free syntheses of ZnO nanowires or nanorods, using several methods, such as thermal chemical vapor deposition (CVD) [3], metal organic chemical vapor deposition [4], molecular beam epitaxy [5], and hydrothermal growth (HG) [6] have been reported. Among these methods, HG and CVD are mostly used for synthesizing ZnO-based nanostructures.

The synthesized ZnO nanowires or nanorods are grown vertically or randomly inclined to the substrate surfaces. In general, vertical ZnO nanorods are usually grown by employing a catalyst, such as Au [7]. However, a catalyst-free process is preferred because of its simplicity and convenience in future device applications. As an alternative, instead of a metal catalyst, ZnO seed layers are frequently used to produce vertically grown ZnO on Si substrates, on which the ZnO seed layers are grown by sputtering or general thin film deposition techniques [8,9], although there are a few reports on the vertical growth of ZnO nanorods on Si substrates without using any seed layer [10]. Here, thin film-based ZnO layers are mostly used as seed layers for ZnO nanowires or nanorod synthesis, but the *intentional* application of ZnO nanorods as an alternative seed or template for re-growth of ZnO nanorods has not been tried.

The aqueous solution-based HG, in which zincnitratehexahydrate [$Zn(NO_3)_2 6H_2O$] solution mixed with hexamethylentetramine [$(CH_2)_6N_4$] solution is generally used as the precursor material to synthesize ZnO nanowires or nanorods [11], is the simplest process compared with other methods. The CVD is an alternative technique in preparing ZnO nanowires, in which ZnO powders mixed with carbon powders are normally used as source materials to grow ZnO nanowires or nanorods [12].

In this study, we tried a combination of HG and CVD processes to grow high-quality ZnO nanorods, in which ZnO nanorods with a diameter of hundreds of nanometers and grown by HG were used successfully as templates for the regrowth of ZnO nanorods by CVD. Vertical ZnO nanorods with high optical properties were synthesized by CVD on ZnO nanorod grown by HG. CVD-re-grown ZnO nanorods showed superior optical quality without deep-level emissions compared with vertical ZnO nanorods grown solely by HG or

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CVD. The results imply that ZnO nanorods themselves can be used as promising seeds or templates for high-quality ZnO nanorods.

2. Experimental details

The substrate used in this study was commercial (1 0 0) Si with a 200-nm-thick SiO_2 layer formed by wet oxidation. Because the removal of the native oxide layer on the Si substrate is practically difficult, the substrates with SiO_2 layer were used to exclude unwanted variations in samples caused by the native oxides. A series of ZnO nanorods were synthesized by HG, CVD, and both HG and CVD, including nanorods grown through a single step by HG, and a double step by HG and CVD. In growing ZnO nanorods, a ZnO seed layer (about 200 nm thick) deposited by sputtering at 500 °C is either used or not. In the ZnO seed layer deposition, radio frequency magnetron sputtering is used.

In the synthesis of ZnO nanorods by HG, precursors of 0.1 M $Zn(NO_3)_2 6H_2O$ and 0.1 M $(CH_2)_6N_4$ mixed at a 1:1 ratio were used [13]. The ZnO nanorod synthesis by HG was performed at 95 °C for 3 h. The aqueous solution with the precursors started the chemical reactions at 60 °C, and the overall reactions can be expressed as follows [14]:

$$(CH_2)_6N_4 + 6H_2O \leftrightarrow 6CH_2O + 4NH_3$$

$$Zn(NO_3)_2 \rightarrow Zn^{2+} + 2NO_3{}^-$$

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

$$Zn^{2+} + 4NH_3 \rightarrow Zn(NH_3)_4{}^{2+}$$

$$Zn^{2+} + 4OH^- \rightarrow Zn(OH)_4{}^{2-}$$

$$Zn(OH)_4{}^{2-} \rightarrow ZnO + H_2O + 2OH^-$$

The CVD growth of the ZnO nanorods was done using the chemical vapor transport method, in which a mixture of ZnO and carbon powders (1:1 wt.%) was used as source material. An alumina boat with the source material is placed at the center of the reactor. Argon gas with a flow rate of 200 sccm was supplied as the carrier gas in the horizontal alumina reactor during heating. As soon as the temperature at the center of the reactor reached 1000 °C, 10 sccm of O_2 gas was supplied and maintained for 20 min to synthesize the nanorods. During the synthesis, the reactor pressure was maintained to 10 Torr by adjusting the orifice to the pumping line. The substrate was placed in a position where the temperature is maintained at 580 °C. The overall reactions during the CVD process for the ZnO nanorod growth can be expressed as follows [15]:

$$ZnO + C \rightarrow Zn + CO$$

$$Zn + O_2 + CO \rightarrow ZnO + CO_2$$

$$Zn + 1/2\,O_2 \rightarrow ZnO$$

The morphology of the synthesized samples was investigated using a field-emission scanning electron microscope (FESEM). Structure and crystallinity were addressed using X-ray diffraction (XRD). Optical property was investigated using room temperature photoluminescence (RT-PL). An He–Cd laser (325 nm line) was used for the excitation source in the photoluminescence (PL) measurements.

3. Results and discussion

Fig. 1 shows the plan view of the FESEM image of the ZnO nanorods grown by HG on SiO_2/Si (0 0 1) substrate without a sputtered ZnO seed layer. As shown in Fig. 1, nanorods with a hexagonally shaped cross-section are synthesized. The nanorods are randomly directed to the substrate surface and verticalness to the surface is not favorable. In addition, the density of the nanorods does not seem high enough. The diameters of the nanorods range from 50 to 600 nm.

To grow ZnO nanorods vertically, ZnO seed layers are normally employed in the CVD synthesis of ZnO nanorods [8,9], although a successful vertical growth without seed layers is possible [10]. Therefore, we employed a ZnO seed layer in synthesizing the ZnO nanorods by HG. Fig. 2(a) shows the plan view of the FESEM image of the sputtered ZnO seed layer grown on a SiO_2/Si substrate. In Fig. 2(a), the grains of ZnO with faceted top surfaces are shown. Grain sizes range roughly from 20 to 80 nm. Fig. 2(b) shows the XRD (θ–2θ) scan from the sputtered ZnO layer. As shown in Fig. 2(b), the ZnO (0 0 2) peak is dominant with the substrate peak, indicating that the sputtered ZnO layer is textured in the preferred (0 0 2) direction.

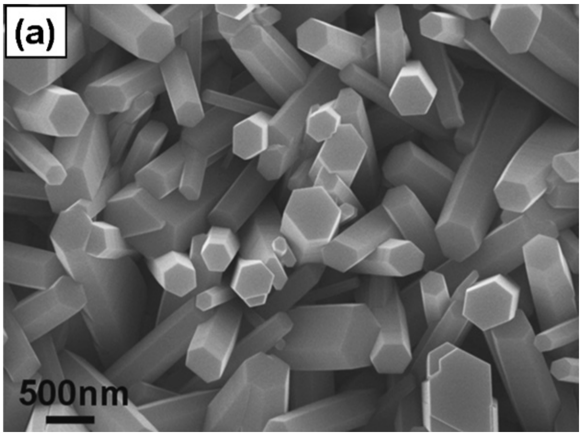

Fig. 1. Plan view FESEM image of ZnO nanorods grown on SiO_2/Si (1 0 0) substrate by HG.

Fig. 3(a) and (b) shows the plan view and cross-sectional FESEM images of ZnO nanorods grown by HG using the substrate with the sputtered ZnO seed layer. Compared with the nanorods grown on a bare substrate without a ZnO seed layer (Fig. 1), the density of the nanorods synthesized on a seed layer is much higher. The diameters of the nanorods range from 50 to 300 nm, and the length is about 1.2 μm, indicating that the seed layer enhances the nucleation of the ZnO nanorods. In addition, as shown in Fig. 3, the nanorods are vertically well aligned to the substrate surface. Figs. 1 and 3 show that the ZnO seed layer is useful in promoting the vertical growth of ZnO nanorods and in increasing density in the synthesis of ZnO nanorods by HG, similar to the CVD process.

Here, the nanorods grown by HG on the sputtered seed layer are very closely arranged to each other, vertically arranged with almost the same height, and with a flat top surface (Fig. 3). Moreover, the diameters of the nanorods, which range from 50 to 300 nm, are larger than the grain sizes of the sputtered seed layer. Although the closely packed nanorods did not form a continuous layer, we infer that the nanorods grown by HG in Fig. 3 can be good alternative seed layers compared with the sputter-deposited seed layer [Fig. 2(a)], which has a rougher surface than the top surface of the nanorods.

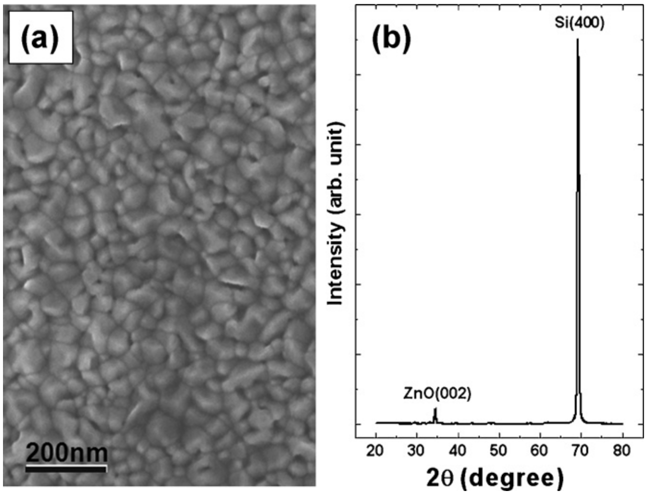

Fig. 2. (a) Plan view FESEM image of ZnO seed layer prepared by sputtering on SiO_2/Si (1 0 0) substrate and (b) XRD θ–2θ scan of the sample.

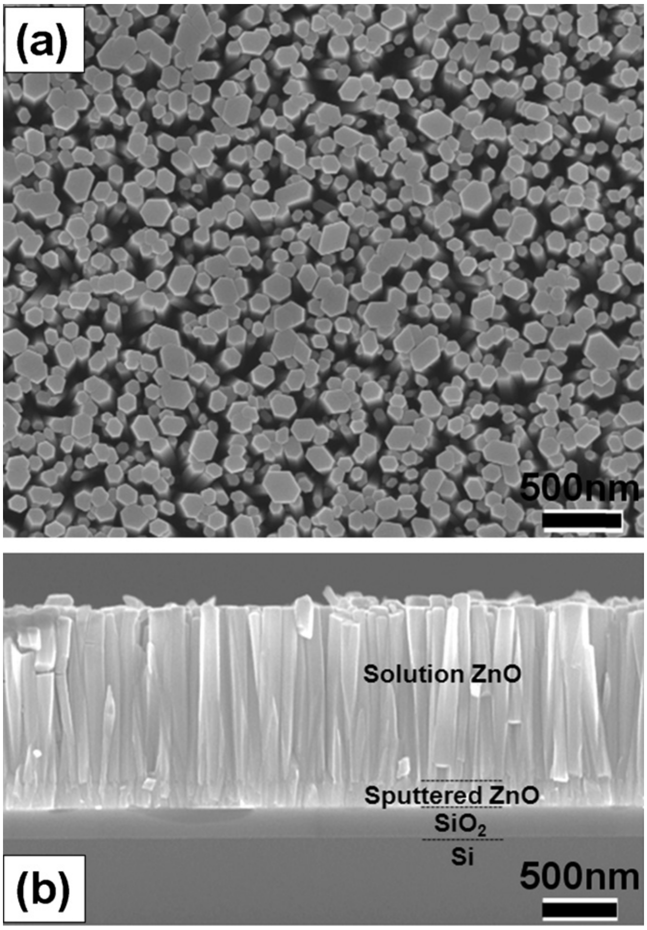

Fig. 3. (a) Plan view and (b) cross-sectional FESEM images of ZnO nanorods grown on the sputtered ZnO seed layer by HG.

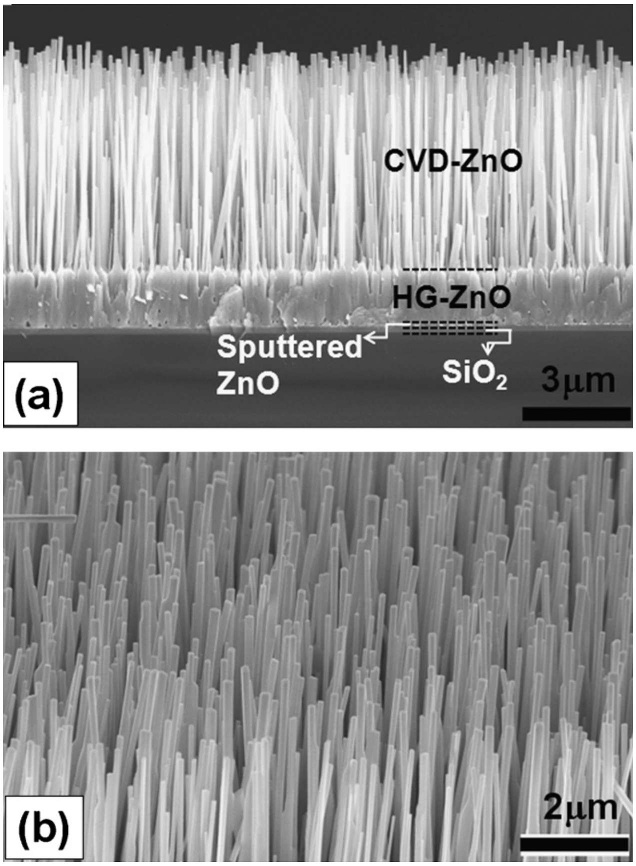

Fig. 4. (a) Cross-sectional FESEM image of ZnO nanorods grown on the HG-prepared ZnO nanorods (the sample shown in Fig. 3) by CVD. (b) Bird-eye view of the nanorods.

Thus, we synthesized the ZnO nanorods by CVD on the nanorods prepared by HG.

Fig. 4 shows ZnO nanorods grown by CVD on ZnO nanorods grown by HG on a sputtered seed layer. As shown in Fig. 4, well aligned vertical ZnO nanorods are re-grown on hydrothermally grown ZnO nanorods. This signifies that the nanorods in Fig. 3 prepared by HG, as expected, acted as a good seed layer. The diameter of the nanorods re-grown by CVD in Fig. 4 is about 120 nm and their length is about 6 μm.

To compare the differences in the properties of the CVD-synthesized nanorods on the new seed material of HG-prepared nanorods with those on the sputtered ZnO seed layer, ZnO nanorod samples are prepared on the sputtered ZnO seed layer. Fig. 5 shows the FESEM images of ZnO nanorods grown by CVD on the sputtered ZnO seed layer. The nanorods grow well vertically on substrates, as shown in Fig. 5. The diameter of the nanorods is about 110 nm and their length is about 5 μm, which is similar to the values for the ZnO nanorods on the new seed material. Considering that both kinds of nanorods (Figs. 4 and 5) are vertical to the substrate surface, XRD (θ–2θ) scans reveal dominant ZnO (0 0 0 2) peaks in addition to the Si (4 0 0) substrate peak, as shown in Fig. 6. However, comparing the relative intensities from the substrate peak intensity in each sample, the intensity of the ZnO (0 0 0 2) peaks from the ZnO nanorods on the HG-prepared nanorod seed material is higher than that from the ZnO nanorods on the sputtered seed layer. This might imply that the crystal quality of ZnO nanorods grown on very flat HG-prepared nanorod seed material is better than that of ZnO nanorods on a sputtered seed layer.

To investigate further the property differences, PL measurements were performed. Fig. 7 shows the RT-PL spectra from several samples. Sample (a) represents ZnO nanorods grown by CVD on HG-prepared nanorod seed material, whereas sample (b) represents ZnO nanorods grown by CVD on sputtered ZnO seed layer. Sample (c) corresponds to nanorods grown by HG on sputtered ZnO seed layer on SiO_2/Si (0 0 1) substrate. Because the CVD process naturally makes thermal annealing during the synthesis, we want to exclude the thermal factor, at least, in comparing the properties of HG-prepared and CVD-prepared ZnO nanorods. Thus, annealing of sample (c) is performed at 500 °C under oxygen ambient for 1 h to evaluate the possible annealing effects on nanorods grown by HG. The annealed sample is represented by sample (d) in Fig. 7. Because the intensity of PL peaks differed up to four orders of magnitude, depending on whether the nanorods were prepared by CVD or HG, the integration time was adjusted to 0.02 s for samples (a) and (b), and 2.5 s for samples (c) and (d). The overall intensities are calibrated, with regard to the integration time, by multiplying the proper factors with the inverse of the respective integration times. The difference in the background noise level is caused by these factors. Here, the difference in the overall thickness of the samples does not have any influence on the resultant PL intensity because the thicknesses of all the samples are much larger than the penetration depth of the excitation laser (<100 nm) [16].

As shown in Fig. 7, the overall PL spectra are composed of two components, namely, near-band-edge emissions at about 380 nm and very broad deep-level emissions at around 530–570 nm. Surprisingly, sample (a) shows negligible deep-level emission compared with sample (b). This indicates that the optical quality of CVD-prepared ZnO nanorods on the new HG-prepared seed mate-

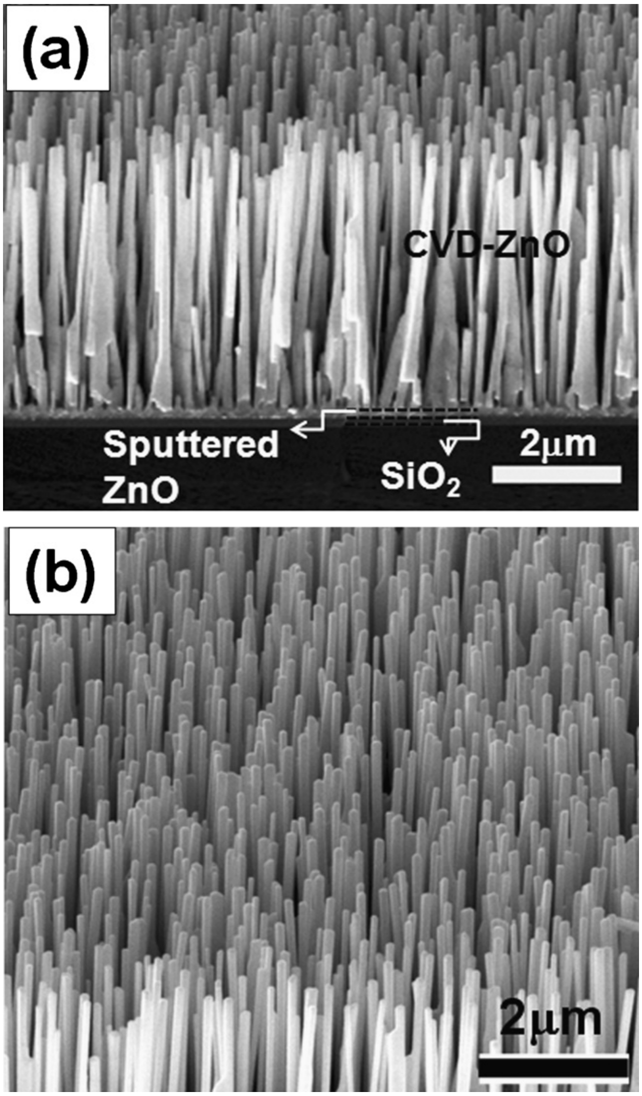

Fig. 5. (a) Cross-sectional FESEM image of ZnO nanorods grown on the sputtered ZnO seed layer (the sample shown in Fig. 2) by CVD. (b) Bird-eye view of the nanorods.

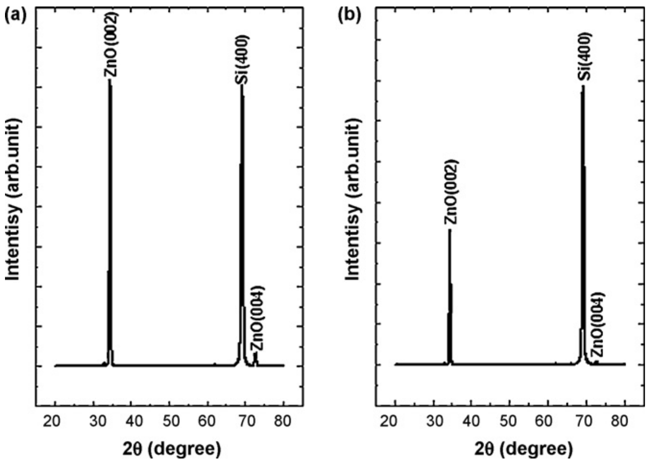

Fig. 6. XRD θ–2θ scan results for the CVD-prepared ZnO nanorods on (a) the HG-prepared ZnO nanorods (the sample shown in Fig. 3) and on (b) the sputtered ZnO seed layer (the sample shown in Fig. 2).

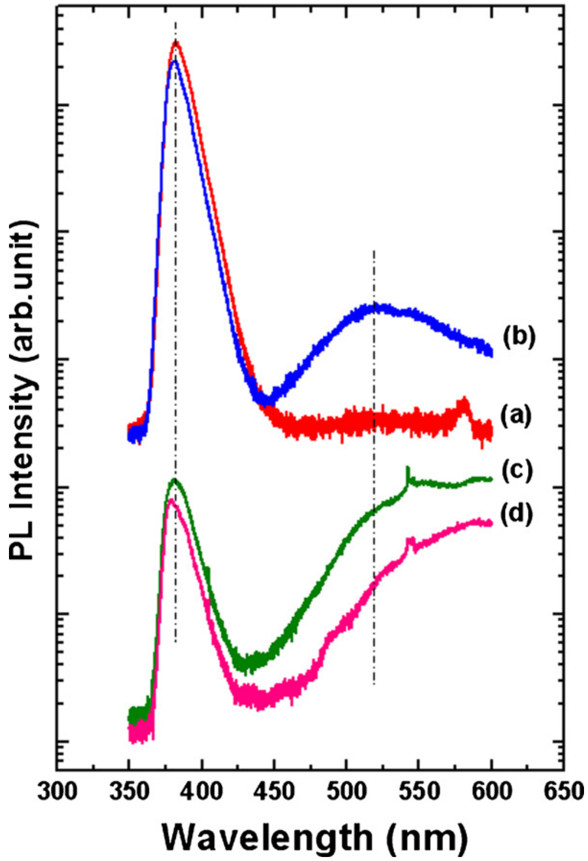

Fig. 7. Room temperature PL spectra from the samples prepared by (a) CVD-prepared ZnO nanorods on the HG-prepared ZnO nanorods on sputtered seed layer, (b) CVD-prepared ZnO nanorods on the sputtered seed layer, (c) HG-prepared ZnO nanorods on sputtered seed layer, and (d) annealed sample of (c) at 500 °C under the oxygen ambient for 1 h.

rial is superior to that on the sputtered ZnO seed layer, although both CVD-prepared ZnO nanorods show similar shapes and crystalline quality. The intensity ratio of the near-band-edge emission (I_{NBE}) to the deep-level emission (I_{DL}) from sample (a) is about 910 but that from the sample (b) is about 151. The intensity ratio of I_{NBE} to I_{DL} is summarized in Table 1.

In Fig. 7, the PL spectrum from sample (c) is shown. The optical properties of ZnO nanorods grown by HG are less favorable than the ZnO nanorods grown by CVD. The HG-prepared nanorods show much weaker near-band-edge emissions and stronger deep-level emissions. Annealed sample (d) shows a similar PL spectrum to sample (c), as shown in Fig. 7. Therefore, the better optical properties of the CVD-nanorods (i.e., sample (a) and (b)) compared with the HG-nanorod (sample (c)) can be understood as the sample property, not the simple annealing effect of CVD-nanorods in the CVD process. The intensity ratios of I_{NBE} to I_{DL} from samples (c) and (d) are 1.0 and 1.5, respectively. In Fig. 7, two vertical lines are drawn to compare the positions of near-band-edge and deep-level emissions

Table 1
Summary of the intensity ratio of near band edge emission (I_{NBE}) to deep level emission (I_{DL}) for four samples in Fig. 5.

Sample	I_{NBE}/I_{DL}
(a) CVD/HG/ZnO seed layer/SiO_2	910.3
(b) CVD/ZnO seed layer/SiO_2	150.9
(c) HG/ZnO seed layer/SiO_2	1.0
(d) Annealed sample of (c)	1.5

from the samples. The positions of the near-band-emissions are almost the same between 382.1 and 379.8 nm. However, the positions of deep-level emissions clearly differ for the CVD-nanorods and the HG-nanorods. This implies that densities and types of structural defects causing the deep-level emissions differ between the ZnO nanorods grown by HG and by CVD.

4. Summary

In this study, we combined the HG and the CVD processes to synthesize high-quality vertical ZnO nanorods. No vertical ZnO nanorods randomly directed to the substrate surface were grown by HG on the SiO_2/Si (1 0 0) substrate without the ZnO seed layer. However, vertically aligned and closely packed ZnO nanorods were grown by HG on a sputtered ZnO seed layer on a SiO_2/Si (1 0 0) substrate. The top surface of these HG-prepared ZnO nanorods showed very flat surfaces compared with that of the sputtered seed layer. Therefore, we used HG-prepared nanorods as a new seed material for CVD growth of ZnO nanorods. Vertical ZnO nanorods were grown by CVD on both the new HG-prepared nanorod seed material and the sputtered ZnO seed layer. However, the CVD-prepared ZnO nanorods on new HG-prepared nanorod seed material showed better crystalline properties and superior optical properties with negligible deep-level emissions than the CVD-prepared ZnO nanorods on sputtered seed layer. The overall RT-PL spectra were composed of two components, namely, near-band-edge emissions at about 380 nm and very broad deep-level emissions at around 530–570 nm. The intensity ratio of I_{NBE} to I_{DL} in the former was about 910, whereas, in the latter, was about 151. This implies that the HG-prepared ZnO nanorods are promising new seed material for nanostructure synthesis. Compared with the vertical ZnO nanorods synthesized by HG and CVD, the ZnO nanorods grown by CVD showed much better optical properties than the nanorods grown by HG, as shown by the RT-PL in the viewpoints of higher orders-of-magnitude I_{NBE} and smaller I_{DL}.

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