

# Improving the property of ZnO nanorods using hydrogen peroxide solution

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## Abstract

Zinc oxide (ZnO) nanorod arrays made by the hydrothermal method were treated with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) solution through two different approaches. One is to immerse ZnO nanorod sample into H<sub>2</sub>O<sub>2</sub> solution. The other is a pre-treatment of spin-coating H<sub>2</sub>O<sub>2</sub> solution on the seed layer before the growth of the ZnO nanorods. In the first approach, we found that the ultraviolet (UV) emission peak of the ZnO nanorod photoluminescence (PL) spectra was strongly dependent on the immersion time. In the second approach, the H<sub>2</sub>O<sub>2</sub> solution influences not only the quality of the seed layer, but also the amount of the oxygen interstitial defects in the ZnO nanorods grown thereon. As a result, the UV emission intensity from the ZnO nanorods is enhanced almost five times. The ZnO nanorod arrays with few oxygen interstitial defects are prepared by the hydrogen peroxide treatment and expected to enable the fabrication of optoelectronic device with excellent performance.

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## 1. Introduction

Zinc oxide (ZnO) is a II–VI semiconductor that demonstrates great potentials for use in blue-ultraviolet (UV) semiconductor lasers [1], light emitting diodes [2–5], and other optoelectronic devices. It has direct wide band gap energy of 3.37 eV at room temperature [6] and strong UV emission due to its large exciton binding energy of 60 meV, which is much larger than that of gallium nitride (25 meV) [7]. In addition, ZnO has no toxicity, involves inexpensive material sources for fabrication, and has excellent transparency in the visible spectral range. The photoluminescence (PL) spectra of ZnO single crystals, powders, nanostructures, and thin film obtained at room

temperature usually exhibit two bands. One occurs at 380 nm, which is related to free-exciton recombination. The other band, which occurs at 500–600 nm, is called green-yellow emission. In most studies, researchers have attributed the green-yellow emission to intrinsic defects (e.g. zinc interstitials or oxygen vacancies) [7–9]. In addition, the oxygen interstitial defects of ZnO would induce a depletion layer at the surface and decrease the PL efficiency [10]. In some studies, certain treatments were used to modify this phenomenon, like UV-illumination [11], exposure to ethanol gas [10], and heat treatments [9].

In this work, we have investigated the influence of hydrogen peroxide treatment on the point defects and structural defects of ZnO nanorods grown on n-type silicon wafer by hydrothermal process [12–14]. Although hydrogen peroxide treatment on the ZnO thin film had been studied, the influences of H<sub>2</sub>O<sub>2</sub> solution on the ZnO nanorods have not been investigated before. In our investigation, PL of ZnO samples was measured and

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discussed in order to gain further insight into the ZnO nanorods' surface characteristics. We have modified the properties of ZnO-nanorod structure through removing the oxygen interstitial defect density successfully by low-cost and low-temperature hydrogen peroxide treatments, which involve processes of either immersing ZnO nanorods samples into  $\text{H}_2\text{O}_2$  solution or a pre-treatment of spin-coating  $\text{H}_2\text{O}_2$  solution on the seed layer before the growth of ZnO nanorods. We discover that PL intensity varies as a function of the immersion time. These effects are attributed to oxygen desorption through oxidation–reduction reactions of hydrogen peroxide on the ZnO surface. The result of our research could provide a method of improvement for ZnO nanorods structure in fabricating optoelectronic devices.

## 2. Experimental details

### 2.1. Preparation of ZnO nanorod arrays

ZnO nanorod arrays were synthesized from zinc nitrate in an aqueous solution under hydrothermal conditions [12,14]. The procedure consisted of two steps: (1) the seed layer ZnO thin film was prepared by a sol–gel method [15]. In detail, zinc acetate dihydrate [ $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ , Merck, 99.5% purity] was dissolved in the mixed solution of monoethanolamine (MEA) [ $\text{CH}_2(\text{OH})\text{CH}_2(\text{NH}_2)$ , Merck, 99.5% purity] and 2-methoxyethanol (2-MOE) [ $\text{CH}_3\text{O}(\text{CH}_2)_2\text{OH}$ , Merck, 99.5% purity]. The concentration of both  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  and MEA in 2-MOE was 0.5 M and the mixture was stirred at  $60^\circ\text{C}$  for 2 h to form a homogeneous and stable colloid solution. The ZnO thin film was deposited on silicon substrates by spin-coating method first at the speed of 1000 rpm for 20 s and then 3000 rpm for 30 s. The substrates were dried at  $300^\circ\text{C}$  on hotplate for removing the organic residues. (2) The samples were immersed in an aqueous solution (50 mM) of zinc nitrate hexahydrate [ $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , Sigma Aldrich, 98% purity] and hexamethylenetetramine (HMT) [ $\text{C}_6\text{H}_{12}\text{N}_4$ , Sigma Aldrich, 99.5% purity]. The reaction temperature was kept at  $90^\circ\text{C}$  and the growth time was 4 h. Finally, the samples were dipped into deionized water to remove the residual ions and dried in air.

### 2.2. Hydrogen peroxide treatment

Two sets of ZnO nanorod samples, labeled as groups I and II, were treated differently with  $\text{H}_2\text{O}_2$  solution. Samples in group I were immersed in a 30%  $\text{H}_2\text{O}_2$  solution for different immersion times, 15, 30, 45, 60 and 90 min at  $75^\circ\text{C}$ . After this procedure, they were cleaned with deionized water to remove the residual  $\text{H}_2\text{O}_2$  solution and dried in air at  $75^\circ\text{C}$ .

For group II, pre-treatments on the seed layer of ZnO nanorods were performed with spin coating method. A 30%  $\text{H}_2\text{O}_2$  solution was spin-coated on the seed layer before the growth of ZnO nanorods at the speed of

1000 rpm for 20 s and then 3000 rpm for 30 s. Then they were heated at  $75^\circ\text{C}$  for 10 min. Afterwards, ZnO nanorods were grown on the pre-treated seed layer.

The crystal phase and crystalline property were analyzed by X-ray diffraction (XRD) pattern using Cu  $\text{K}\alpha$  radiation. The PL spectra were measured at room temperature by using a Nd:YAG laser at 266 nm as the exciting source to examine the properties of the ZnO seed layer and nanorods.

## 3. Results and discussion

Fig. 1 shows a series of room temperature PL spectra of untreated ZnO nanorods and  $\text{H}_2\text{O}_2$ -treated samples in group I. The sharp UV emission peaks at 383 nm are the dominant peaks in the PL spectra, which originate from the excitonic recombination corresponding to the band edge emission of ZnO. Furthermore, these UV peaks vary with the immersion time of samples in group I. In order to discuss the tendency of the time-dependent UV emission in detail, we plot the UV intensity ratio of samples in group I to untreated ZnO nanorods versus the immersion time. The result is shown as Fig. 2. From this figure, the ratio increases with the time up to 30 min and then starts to decrease as the immersion process continues.

For  $t = 0$ –30 min, the increase in PL intensity implies that more electron–hole pairs recombine through radiative process than through nonradiative means. We attribute the enhancement of PL intensity to the oxygen desorption on the surface of ZnO nanorods and we infer that the reactions are  $\text{O}_i^-/\text{O}_i^{2-} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}_{2(\text{g})} + \text{e}^-/2\text{e}^-$ . It is believed that the interstitial oxygen ions ( $\text{O}_i^-$  and  $\text{O}_i^{2-}$ ) provide surface defect states to trap photogenerated holes, and thus the electron–hole pairs tend to recombine nonradiatively. As the oxygen is removed from the ZnO surface, fewer centers of nonradiative recombination lead to an increase in PL intensity. In addition,  $\text{O}_i^-$  and  $\text{O}_i^{2-}$  induce a depletion layer under the surface of ZnO. Because the electrons and holes move to opposite direction under

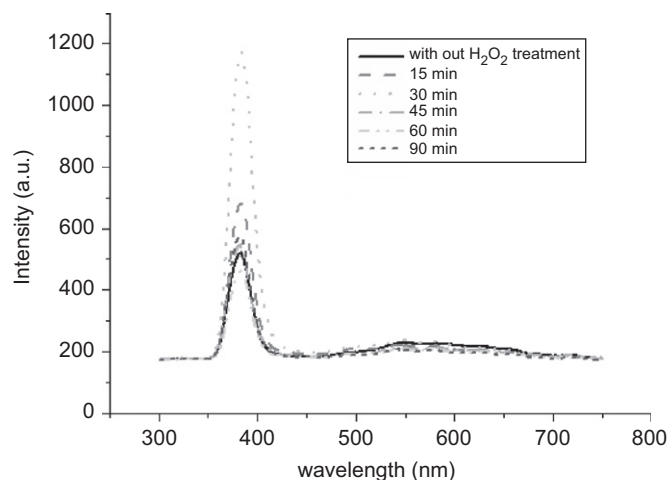


Fig. 1. PL spectra of samples in group I at room temperature for different immersion time.

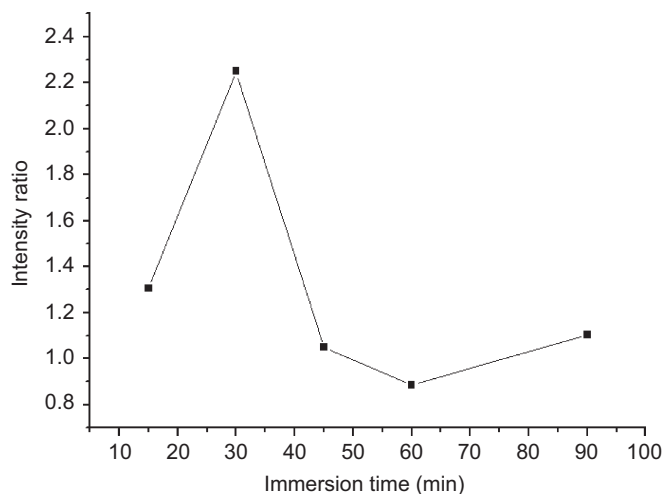


Fig. 2. The UV emission intensity ratio of samples in group I to untreated ZnO nanorods depending on the immersion time.

an electric field induced in the depletion layer, the probability of forming excitons is decreased. The increase in PL intensity can be also viewed as a result of the reduction in depletion width. Furthermore, the ZnO nanorods have a large surface area to volume ratio, and the influence of above mechanisms on nanorods is more obvious. Additional experimental evidence for the effect of hydrogen peroxide treatment is given in Fig. 3. This figure shows the FTIR spectra of the untreated ZnO nanorods and the ZnO nanorods immersed in  $\text{H}_2\text{O}_2$  solution for 15 min in the range of  $600\text{--}1800\text{ cm}^{-1}$ . The peaks at  $1416$  and  $1330\text{ cm}^{-1}$  are associated with bending of OH [16,17]. Because the samples were immersed in the water during the growth of ZnO nanorods, the oxygen adsorbed to the surface would rather become O–H. The intensity of the peaks about O–H for ZnO nanorods immersed in  $\text{H}_2\text{O}_2$  solution is smaller than that of untreated ZnO nanorods. Consequently, we can conclude that the oxygen adsorption to the surface of samples is removed by hydrogen peroxide.

For  $t = 30\text{--}60$  min, most oxygen interstitial defects on the surface have been removed but the hydrogen peroxide still continue to release oxygen. The reaction  $\text{O}_i^-/\text{O}_i^{2-} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}_{2(g)} + e^-/2e^-$  cannot proceed because of lacking  $\text{O}_i^-$  and  $\text{O}_i^{2-}$ . The oxygen resulting from the decomposition of hydrogen peroxide will adsorb on the ZnO surface and ionize to become  $\text{O}_i^-$  and  $\text{O}_i^{2-}$  by extracting electrons from ZnO conduction band;  $\text{O}_i^-/\text{O}_i^{2-} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}_{2(g)} + e^-/2e^-$  [10], and  $\text{O}_i^-$  is believed to be dominant [18]. Consequently, the depletion layer is formed in the surface and in the grain-boundary of ZnO and reduces the UV emission again.

For  $t = 60\text{--}90$  min, the oxygen ions accumulate enough to react with hydrogen peroxide. As oxygen adsorption is removed again, the UV emission will start to increase. The amounts of  $\text{O}_i^-$  and  $\text{O}_i^{2-}$  affect the behavior of  $\text{H}_2\text{O}_2$ . However,  $\text{H}_2\text{O}_2$  can only react with the oxygen near the ZnO surface. In other words, the  $\text{O}_i^-$  and  $\text{O}_i^{2-}$  inside of ZnO cannot be removed by  $\text{H}_2\text{O}_2$ ; so we try to restrain the

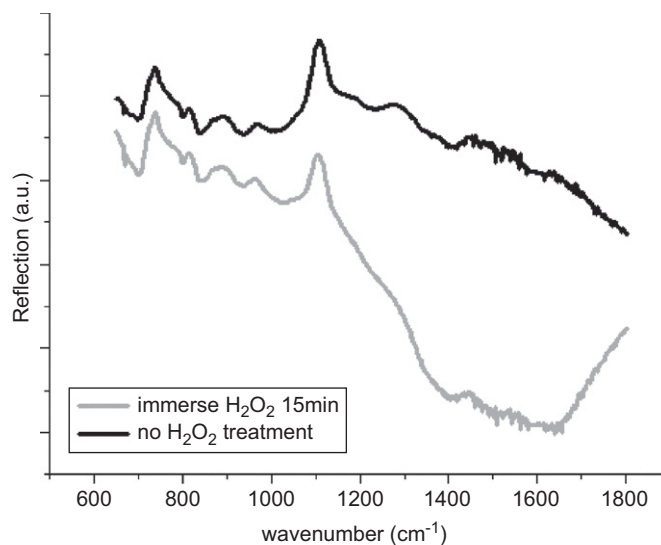


Fig. 3. FTIR reflection spectra of the ZnO nanorods immersed in  $\text{H}_2\text{O}_2$  for 15 min and untreated ZnO nanorods.

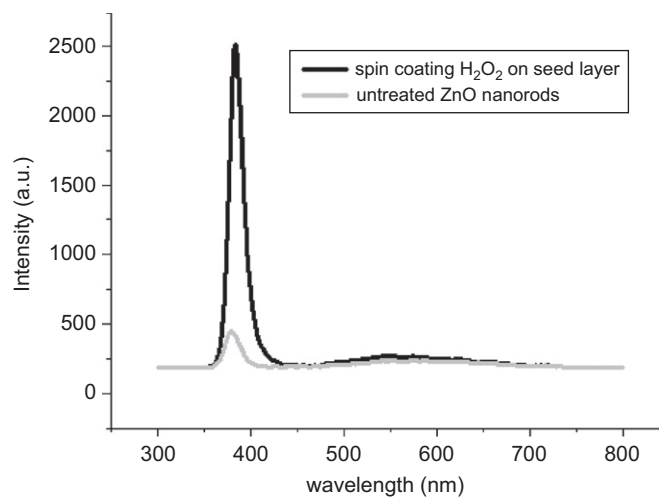


Fig. 4. PL spectra of samples in group II at room temperature for different approaches.

production of  $\text{O}_i^-$  and  $\text{O}_i^{2-}$  by applying  $\text{H}_2\text{O}_2$  treatment on the seed layer of ZnO nanorods during the formation of ZnO nanorods.

Fig. 4 shows a series of PL spectra of samples in group II.  $\text{H}_2\text{O}_2$  solution had been spin-coated onto the seed layer before the growth of ZnO nanorods. From this figure, a strong UV emission peak, which is almost five times the intensity of untreated ZnO nanorods, is observed. The increase in PL intensity can be viewed as a result of few oxygen interstitial defects. As  $\text{H}_2\text{O}_2$  solution is spin-coated on the seed layer of ZnO nanorods, it removes  $\text{O}_i^-$  and  $\text{O}_i^{2-}$  of the seed layer. It is suggested that the seed layer likely reduce the  $\text{O}_i^-$  and  $\text{O}_i^{2-}$  density and less lattice distortion stress exists during the growth of ZnO nanorods. Therefore, the structure of ZnO nanorods has fewer defects and the probability of forming excitons increases. The pre-treatment of seed layer has excellent performance on the reduction of oxygen interstitial defects for ZnO structure.

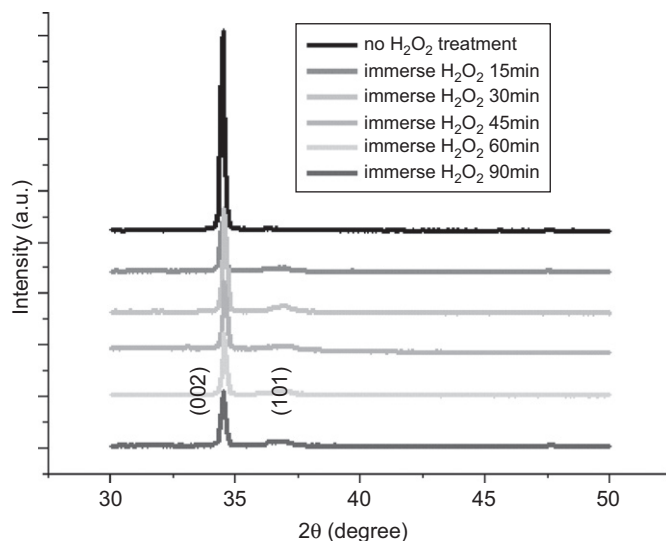


Fig. 5. XRD pattern of the samples in group I.

Fig. 5 shows the XRD patterns for samples in group I before and after immersion in 30%  $\text{H}_2\text{O}_2$  solution. It is found that no other characteristic peaks corresponding to the precursors such as zinc nitrate and zinc hydroxide are observed in Fig. 5. The dominant (002) peak of XRD patterns shows that the samples are all of high  $c$ -axis orientations. The intensity of (002) peak for samples in group I gradually decreases with the immersion time up to 90 min. At the same time, these samples have a very weak (101) peak as the immersion time increases. The study of Chen et al. [19] has suggested that the thicker ZnO film has the better crystalline quality during the growth of the film. This means that the ZnO crystalline property of the lower layer is worse than that of the upper layer. Because the growth mechanism of ZnO films and ZnO nanorods is similar, the ZnO nanorods have better crystalline quality at the external portion than at the internal portion. This tendency is similar to that of ZnO films. From the result of XRD measurement, we infer that there are more dislocations of  $\text{Zn}^{2+}$  or  $\text{O}^{2-}$  related (002) and (101) plane at the internal portion of ZnO than at the external portion. As the external portion was etched off by 30%  $\text{H}_2\text{O}_2$  solution with a pH of 3–4, the uncovered dislocations caused the change of XRD pattern in samples in group I. This tendency can explain the decrease of the intensity in (002) peak and the increase of the intensity in (101) peak for samples in group I as the immersion time increases. In comparison with the weak (101) peak, the sharp (002) peak is relatively strong, suggesting that the hydrogen peroxide treatment does not noticeably reduce the crystal quality of ZnO nanorods. This result indeed reflects that the PL spectra is mainly caused by desorption of surface oxygen instead of the change of the structure property.

#### 4. Conclusions

In conclusion, we report here a simple and inexpensive method for improving ZnO-nanorod structure quality by

removing oxygen interstitial defects. We observe a UV emission enhanced PL in the samples immersed in hydrogen peroxide. This change of luminescent properties is mainly related to desorption of the surface oxygen and the reduction of the depletion layer width. From the result of FTIR measurement, we confirm that  $\text{H}_2\text{O}_2$  can remove the oxygen adsorbed to ZnO surface. The change of crystalline properties of the samples in group I is due to the different properties of external and internal portions in ZnO nanorods. In addition, the UV emission at 383 is enhanced almost five times by pre-treatment on the seed layer with spin-coating  $\text{H}_2\text{O}_2$  solution. Therefore, this could be an excellent technique providing a route to fabrication of low-cost and high quality ZnO nanorods with only few oxygen interstitial defects for applications.

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