

PAPER

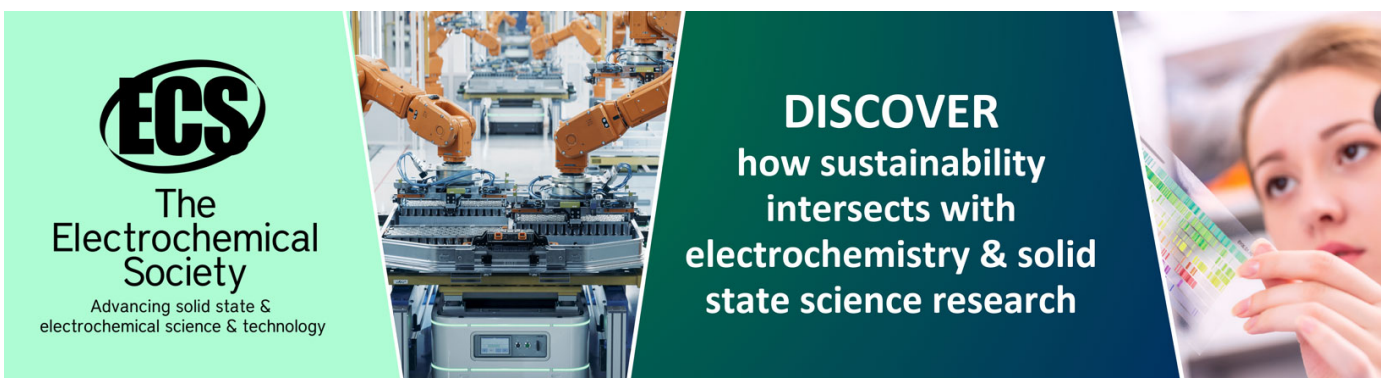
## Study of near white light emission for ZnO thin films grown on silicon substrates

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# Study of near white light emission for ZnO thin films grown on silicon substrates

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## Abstract

ZnO thin films at growth time of 6, 8, 10 and 12 h were prepared by hydrothermal approach. The microstructure, surface morphology and photoluminescence properties were investigated by x-ray diffraction, field-emission scanning electron microscope and fluorescence spectrometer. The results reveal that all the thin films have hexagonal wurzite structure and preferential orientation along the *c*-axis. The density of nanorods increases first and then decreases with the increase of growth time. The photoluminescence spectra consist of sharp near band-edge, broad visible and near-infrared emissions. The chromaticity coordinates and color rendering indices of ZnO thin film at growth time of 10 h are  $x = 0.3537$ ,  $y = 0.3744$  and 90, respectively. The mechanisms of the green, yellow, orange-red, red and near-infrared emissions were discussed in detail.

## 1. Introduction

ZnO has a wide band gap ( $\sim 3.37$  eV at room temperature) and high exciton binding energy (60 meV), which assure stable excitonic emission even above room temperature [1, 2]. ZnO typically exhibits one emission peak in the UV region due to the recombination of free excitons, and possibly one or more peaks in the visible spectral range which are attributed to defect emissions [3, 4]. In addition, the red and near-infrared (NIR) emissions in ZnO have been investigated by many researchers [4–7]. Owing to these properties, ZnO has attracted increasing attention as a promising candidate material for potential applications in optoelectronic devices. Experimental results showed that the emissions of ZnO were dominated by preparation methods [8, 9], substrate [9], post-processing [10] and so on. So far, the origin of defect emissions is

still not fully clear. More recently, the white light emission of ZnO due to deep defect states in the bandgap has been studied by some researchers [11–13]. Hussain *et al* [11] investigated the white-light luminescence from ZnO organic hybrid light-emitting diodes grown on glass substrate. The mechanism of white emission of In doped ZnO nanoparticles has been discussed by Li *et al* [12]. ZnO nanotubes with white light emission were prepared by Guo *et al* [14]. However, the study of white light emission of ZnO is still in its infancy.

In this work, ZnO thin films with near white light emission have been prepared by a facile hydrothermal approach. A sharp near band-edge (NBE) emission band, a broad visible emission band and a NIR emission band were observed in the photoluminescence (PL) spectra at room temperature. The broad visible emission band consists of green, yellow, orange-red and red emission. The mechanisms of the visible and NIR emission were investigated in detail.

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## 2. Experimental details

In a typical experimental procedure, zinc acetate dehydrate [ $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ] and monoethanol amine (MEA) were dissolved in ethylene glycol monomethyl ether solution at room temperature. The molar ratio of MEA to zinc acetate dehydrate was kept as 1.0. The solution was stirred at  $60^\circ\text{C}$  for 120 min using a magnetic stirrer to get a clear, homogeneous and transparent sol, which served as the coating sol after being kept for 24 h. Silicon wafer was employed as the substrate, and it was cleaned ultrasonically in acetone, rinsed with a large amount of deionized water, and dried in hot air. After spin coating, the substrate was heated at  $150^\circ\text{C}$  for 10 min to remove the solvent and this procedure was repeated twice. The seed was finally post-heated at  $600^\circ\text{C}$  for 60 min in air using an electronic furnace. Growth of ZnO thin film was carried out by suspending the ZnO seed in a 50 mL Teflon-lined stainless steel autoclave filled with 40 mL aqueous solution of zinc nitrate hexahydrate [ $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ] and methenamine [ $\text{C}_6\text{H}_{12}\text{N}_4$ , HMT] at  $95^\circ\text{C}$  for 6, 8, 10 or 12 h in an oven, respectively. Finally, the samples were washed with deionized water and dried in the air at  $60^\circ\text{C}$ .

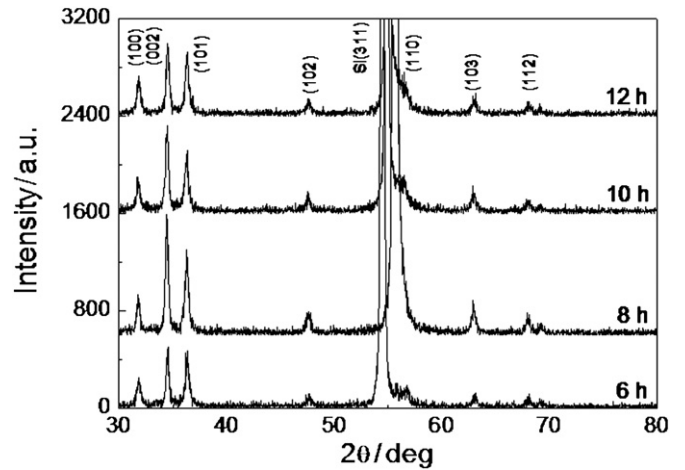
The crystallinity of the ZnO thin films was analyzed by x-ray diffraction (XRD, MACM18XHF) employing Cu K $\alpha$  radiation ( $\lambda = 0.15405\text{ nm}$ ). The preferred growth of the ( $hkl$ ) planes has been expressed in terms of a texture coefficient  $T_{c(hkl)}$ . Quantitative information concerning the degree of preferential orientation can be obtained from the texture coefficient,  $T_{c(hkl)}$ , defined as [15]:

$$T_{c(hkl)} = \frac{I_{(hkl)}/I_{r(hkl)}}{[(\sum I_{(hkl)}/I_{r(hkl)})/n]}, \quad (1)$$

where  $I_{(hkl)}$  are the measured relative intensity of the reflection from the ( $hkl$ ) plane,  $I_{r(hkl)}$  is that from the same plane in standard reference (JCPDS card 36-1451) of the randomly oriented crystallites,  $n$  is the number of diffraction peaks considered. In our case,  $n = 6$ , since six peaks are selected, i.e. (100), (002), (101), (102), (103) and (112). For the extremely preferential orientation,  $T_{c(hkl)} = 6$ , while for the random one,  $T_{c(hkl)} = 1$ . The surface morphologies were determined by the field emission scanning electron microscope (FE-SEM, Hitachi S-4800). The PL spectra of the ZnO thin films were measured at room temperature by fluorescence spectrometer (FL, Horiba Jobin Yvon iHR320) with a Kimmon 1K Series He–Cd Laser as light source excited at 325 nm.

## 3. Results and discussion

XRD patterns of ZnO thin films grown on silicon substrates are shown in figure 1. All the diffraction peaks in figure 1 are in good agreement with the hexagonal phase ZnO (JCPDS 36-1451) except the (311) diffraction peak of cubic phase silicon (JCPDS 27-1402). The texture coefficients,  $T_{c(100)}$ ,  $T_{c(002)}$  and  $T_{c(101)}$  of the ZnO thin films are shown in table 1. The results reveal that all the thin films have a hexagonal wurzite structure and have enhanced intensities for the peaks corresponding to (002) plane, indicating preferential orientation along the  $c$ -axis. It can be seen from table 1 that the texture coefficient



**Figure 1.** X-ray diffraction patterns of ZnO thin films with various growth times.

**Table 1.** Texture coefficients and average crystal size of ZnO thin films.

Growth time (h)	$T_{c(100)}$	$T_{c(002)}$	$T_{c(101)}$	Average crystal size (nm)
6	0.898	2.360	0.889	26.8
8	0.619	2.709	0.799	29.5
10	0.913	2.622	0.663	28.3
12	1.014	2.358	0.885	26.1

$T_{c(002)}$  and average crystal size increase first and then decrease with the increase of growth time. ZnO thin films at growth time of 8 h have the highest degree of preferential orientation along the  $c$ -axis.

Figure 2 shows the FE-SEM images of the thin films. When the growth time is 6 h, the morphology of the thin films mainly contains pencil-like ZnO nanorods. When the growth time increases to 8 and 10 h, the shapes of the nanorods change from pencil-like to hexagonal prism structures. Pencil-like ZnO nanorods appear once again in the thin film grown for 12 h. The density of nanorods increases first and then decreases as the growth time increases. These results demonstrate that the rate of nucleation and nanorods growth is sensitive to the growth time. When the growth time is short, the rate of nanorods growth is higher than that of nucleation. When the growth time increases, the rate of nucleation becomes higher than that of nanorods growth, and hence many fine nanorods are produced. Further increasing the growth time, the rate of nanorods growth is less than that of reversal dissolution process. The nanostructure features of ZnO thin films grown for 12 h may be a result of the evolution of the dissolution [16, 17].

The room temperature PL spectra of ZnO thin films are shown in figure 3. It can be seen that sharp NBE emission, broad visible emission and NIR emission are observed in the PL spectra. The sharp NBE emission can be attributed to the band edge excitonic recombination [18]. Wang *et al* considered that the NIR emission may be caused by the donor–acceptor transition between  $V_O$  and  $V_{Zn}$  and/or the radiative recombination of shallowly trapped electrons with deeply

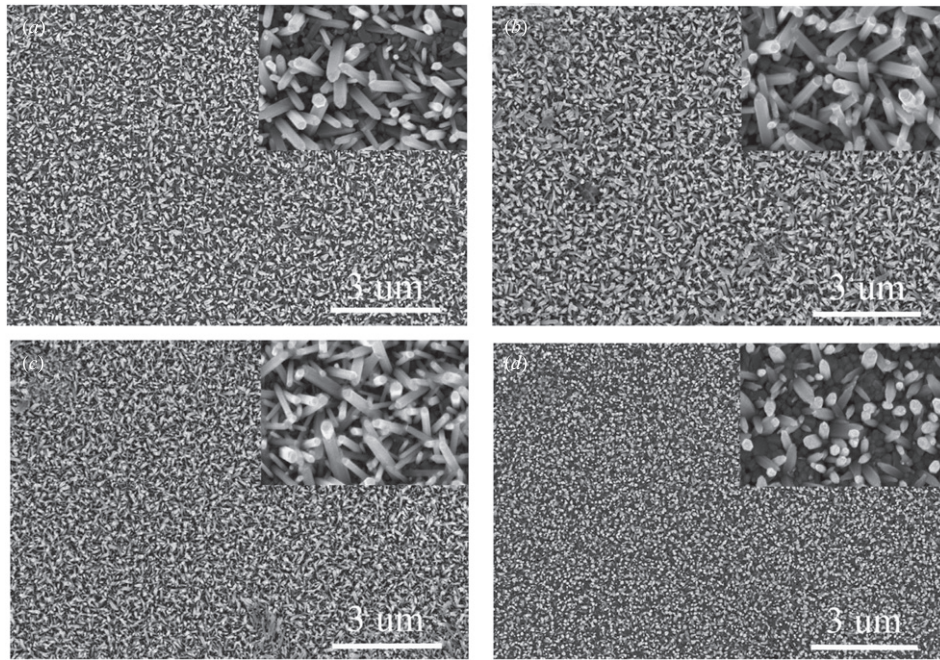


Figure 2. FE-SEM images of ZnO thin films at growth time of (a) 6 h, (b) 8 h, (c) 10 h and (d) 12 h.

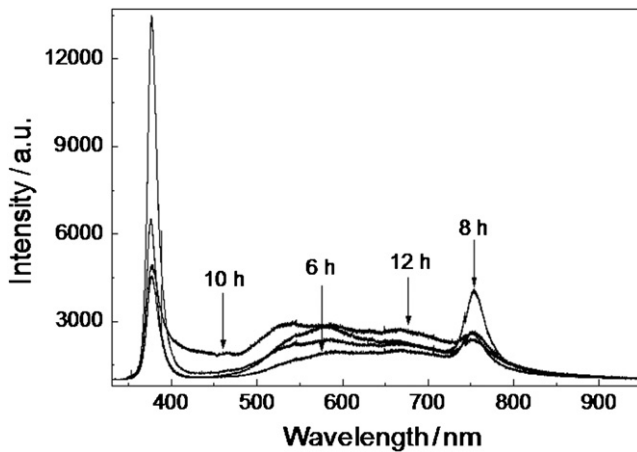


Figure 3. Photoluminescence spectra of ZnO thin films at growth time of 6, 8, 10 and 12 h.

trapped holes at  $O_i$  [19]. However, we thought that the NIR emission in this letter could be ascribed to the second-order diffraction of the NBE emission [20–22]. The strongest NBE emission and NIR emission appear in the ZnO thin film at growth time of 8 h, which may be due to the largest average crystal size and highest degree of preferential orientation along the  $c$ -axis.

According to the PL spectra in figure 3, we calculate the chromaticity coordinates of ZnO thin films using the following formula [23]:

$$\left. \begin{aligned} X &= \int_{380}^{780} \bar{x}(\lambda)p(\lambda)d\lambda \\ Y &= \int_{380}^{780} \bar{y}(\lambda)p(\lambda)d\lambda \\ Z &= \int_{380}^{780} \bar{z}(\lambda)p(\lambda)d\lambda \end{aligned} \right\} \quad (2)$$

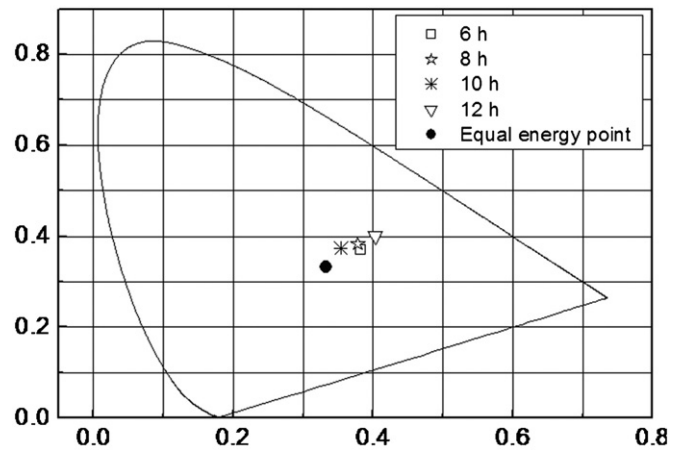
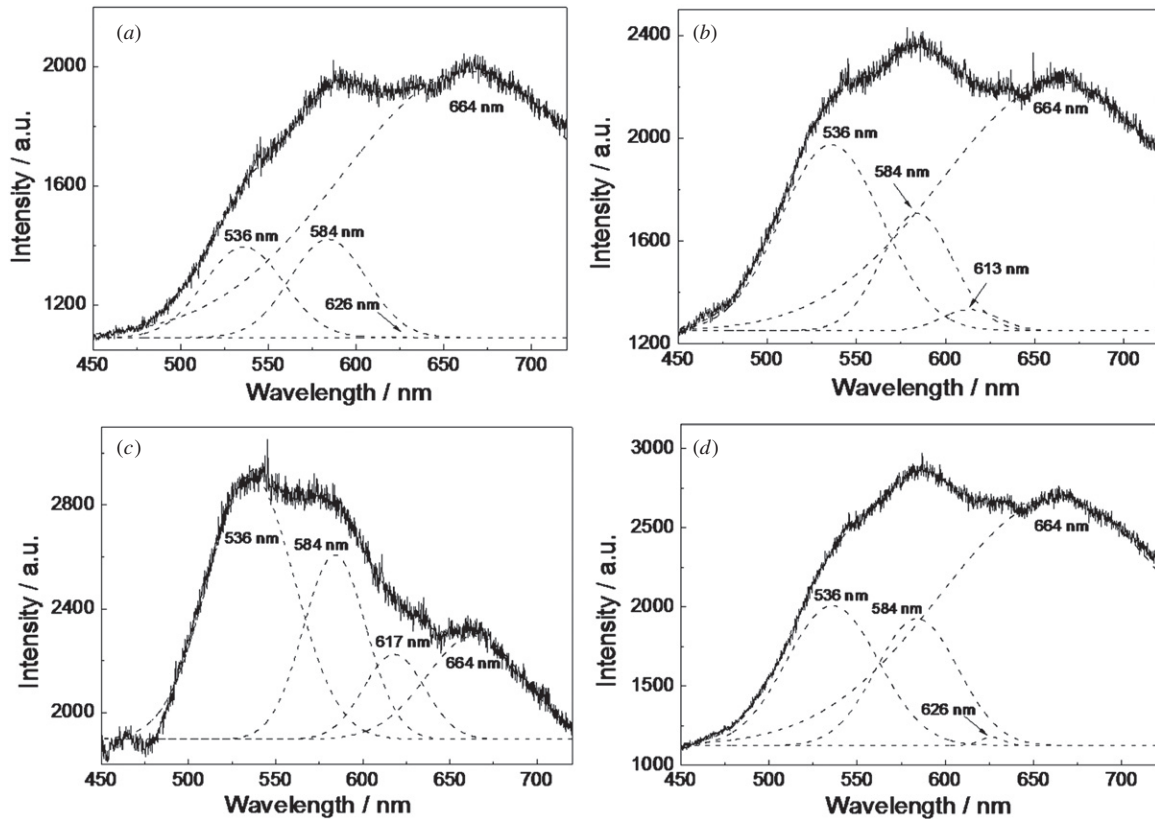


Figure 4. Chromaticity coordinates of ZnO thin films and the equal energy point of white light.

$$\left. \begin{aligned} x &= \frac{X}{X + Y + Z} \\ y &= \frac{Y}{X + Y + Z} \end{aligned} \right\} \quad (3)$$

where  $\bar{x}$ ,  $\bar{y}$  and  $\bar{z}$  are the standard spectral tristimulus values of CIE-1931,  $p(\lambda)$  is the spectral intensity distribution and  $x$ ,  $y$  are the chromaticity coordinates. The calculated results are shown in figure 4. Chromaticity coordinates are (0.3825, 0.3709), (0.3779, 0.3836), (0.3537, 0.3744) and (0.4035, 0.4013), the color rendering indices are 96, 92, 90 and 89 and the correlated color temperatures are 3872, 4098, 4780 and 3585 K, corresponding to ZnO thin films grown for 6, 8, 10 and 12 h, respectively. When the growth time is 10 h, the chromaticity coordinates are very close to the equal energy point of white light. White light luminescence of light-emitting diodes (LED) based on different ZnO nanostructures have been

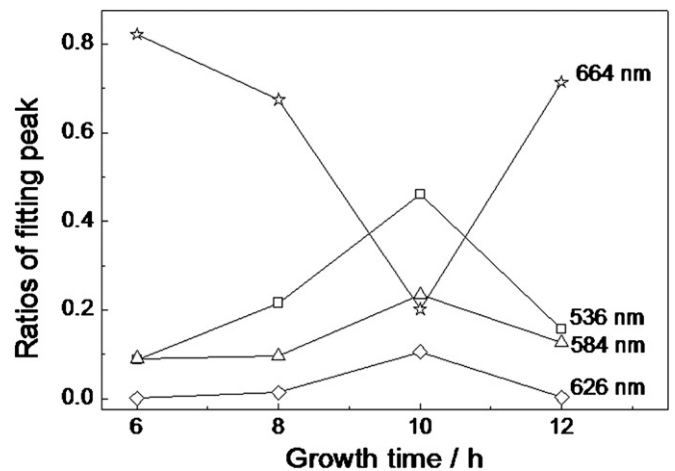


**Figure 5.** The best fitting results of fine visible emission bands of ZnO thin films at growth time of (a) 6 h, (b) 8 h, (c) 10 h and (d) 12 h.

reported by some researchers [24, 25]. White LED based on the ZnO thin film will be further studied in our group.

In order to distinguish the broad visible band components, a Gaussian function was used to simulate experimental data. The PL spectra show four emissions at about 536, 584, 626 and 664 nm which are associated with green, yellow, orange-red and red emissions, respectively. The best fitting results of fine visible emission bands of the ZnO thin films with different growth times are shown in figure 5. The spectral analysis was carried out on the basis of the data presented in the paper and allowed us to draw following conclusions. The green emission in the PL spectra may be attributed to the electron transition from zinc interstitial ( $Zn_i$ ) to oxygen vacancy ( $V_o$ ) defect levels in ZnO [7]. The yellow emission is due to electron transition from conduction band to oxygen interstitial ( $O_i$ ) [26]. The orange-red emissions believed to be due to electron transition from zinc interstitial ( $Zn_i$ ) to oxygen interstitial ( $O_i$ ) [27]. The red emission was recently attributed to transitions associated with zinc vacancy complexes [28].

According to the fitting results, the ratios of area of each fitting peak to that of the whole broad visible band were calculated. The ratios of each fitting peak and its evolution as a function of growth time are shown in figure 6. When growth time increases from 6 to 12 h, the ratio of the red emission decreases first, reaching a minimum of about 0.201 at 10 h, and then increases. Ratios of all the other three emissions increase first, reaching a maximum at 10 h, and then decrease. Thus, the near white light emission of ZnO thin films with 10 h growth time may be related to stronger green, yellow and orange-red



**Figure 6.** Ratios of each fitting peak of ZnO thin films and its evolution as a function of growth time.

emission. The results indicate that as compared with other ZnO thin film, the thin film at growth time of 10 h has more zinc interstitial ( $Zn_i$ ), oxygen vacancy ( $V_o$ ) and oxygen interstitial ( $O_i$ ) defect and less zinc vacancy complexes.

#### 4. Conclusions

In conclusion, ZnO thin films at different growth time have been synthesized by a facile hydrothermal approach. The structure, morphology and optical properties were investigated

by XRD FE-SEM and PL, respectively. The XRD results show that all of the peaks can be attributed to the hexagonal wurzite structure and the preferred *c*-axis orientation increases first and then decreases with the increase of growth time. SEM results indicate that the thin films consist of pencil-like or hexagonal prism ZnO nanorods. PL spectra were mainly composed of one NBE emission, one NIR emission and four visible emissions. The NIR emission of ZnO thin films can be ascribed to the second-order diffraction of the NBE emission. A near white light emission was observed in the ZnO thin film at growth time of 10 h.

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