

# Morphology and optical properties of zinc oxide thin films grown on Si (100) by metal-organic chemical vapor deposition

S. M. Lan · W. Y. Uen · C. E. Chan · K. J. Chang · S. C. Hung ·  
Z. Y. Li · T. N. Yang · C. C. Chiang · P. J. Huang · M. D. Yang ·  
G. C. Chi · C. Y. Chang

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**Abstract** Undoped zinc oxide (ZnO) thin films were deposited on Si (100) substrates by atmospheric pressure metal-organic chemical vapor deposition (AP-MOCVD). After a nucleation layer of ZnO about 500 Å was deposited, top ZnO films with 320–440 nm in thickness were fabricated at temperatures varying from 450 to 600 °C, respectively. X-ray diffraction analyses demonstrate that all the films grown have polycrystalline wurtzite structure. Scanning electron microscopy observations indicate that ZnO films grow with *c*-axis aligned grains when the deposition temperature is lower than 600 °C. However, 3D

microstructures without *c*-axis alignment were found when the film was deposited at 600 °C. Room temperature photoluminescence (PL) spectra peaking at 3.27–3.29 eV were observed for the ZnO films grown at 450–600 °C. However, only the spectrum from the film grown at 600 °C could present a high intensity ratio of the ultraviolet band to deep-level emissions, which is above 392 and show a minimum full-width at half-maximum of 99 meV for the ultraviolet band. Temperature-dependent PL measurements from 20 to 300 K exhibited the luminescent mechanism of the present ZnO films to be near band excitonic emission.

S. M. Lan · T. N. Yang · C. C. Chiang  
Institute of Nuclear Energy Research, P.O. Box 3-11,  
Lung-tan 32500, Taiwan

W. Y. Uen (✉) · C. E. Chan · Z. Y. Li  
Department of Electronic Engineering, College of Electrical  
Engineering and Computer Science, Chung-Yuan Christian  
University, Chung-Li 32023, Taiwan  
e-mail: uenwuyih@ms37.hinet.net;  
top12340099@yahoo.com.tw

K. J. Chang · C. Y. Chang  
Materials & Electro-Optics Research Division,  
Chung-Shan Institute of Science & Technology,  
Lung-Tan, Taoyuan 32599, Taiwan

S. C. Hung · P. J. Huang · G. C. Chi  
Department of Physics, National Central University,  
Chung-Li, Taoyuan 32001, Taiwan

Z. Y. Li  
Department of Photonics & Institute of Electro-Optical  
Engineering, National Chiao Tung University, 1001 Ta Hsueh  
Road, Hsinchu 30010, Taiwan

M. D. Yang  
Department of Physics, Chung-Yuan Christian University,  
Chung-Li 32023, Taiwan

## 1 Introduction

Zinc oxide (ZnO) has a wide direct band gap of 3.37 eV and large free excitonic binding energy of 60 meV [1–4]. It is also a transparent material in the visible-light region and electrically conductive once doped with elements such as aluminum or arsenic. These properties have been studied for applications to transparent conducting electrodes for flat panel displays and solar cells [2, 3]. In addition, the nanostructures of ZnO have recently been investigated quite intensively. Research topics concerned with ZnO nanostructures cover a wide extension including quantum dots (QDs) [5, 6], nanowire [7, 8], nanorod [9], nanopin [10], nanodisk [11], and so on.

In device applications, ZnO has received particular attention as a promising material to be used for ultraviolet light emitting diodes (UV-LEDs) and nanowire UV photodetectors [12]. Several techniques have been used to grow ZnO films, such as pulsed laser deposition (PLD) [4], sputtering and molecular beam evaporation (MBE) [2]. However, little has been known about the growth of ZnO

thin film on Si substrate by atmospheric pressure metal-organic chemical vapor deposition (AP-MOCVD). In this article, we investigate an optimal temperature to grow ZnO on Si by analyzing and comparing the morphologies and crystalline qualities of ZnO films grown at different temperatures ranging from 450 to 600 °C.

## 2 Experimental details

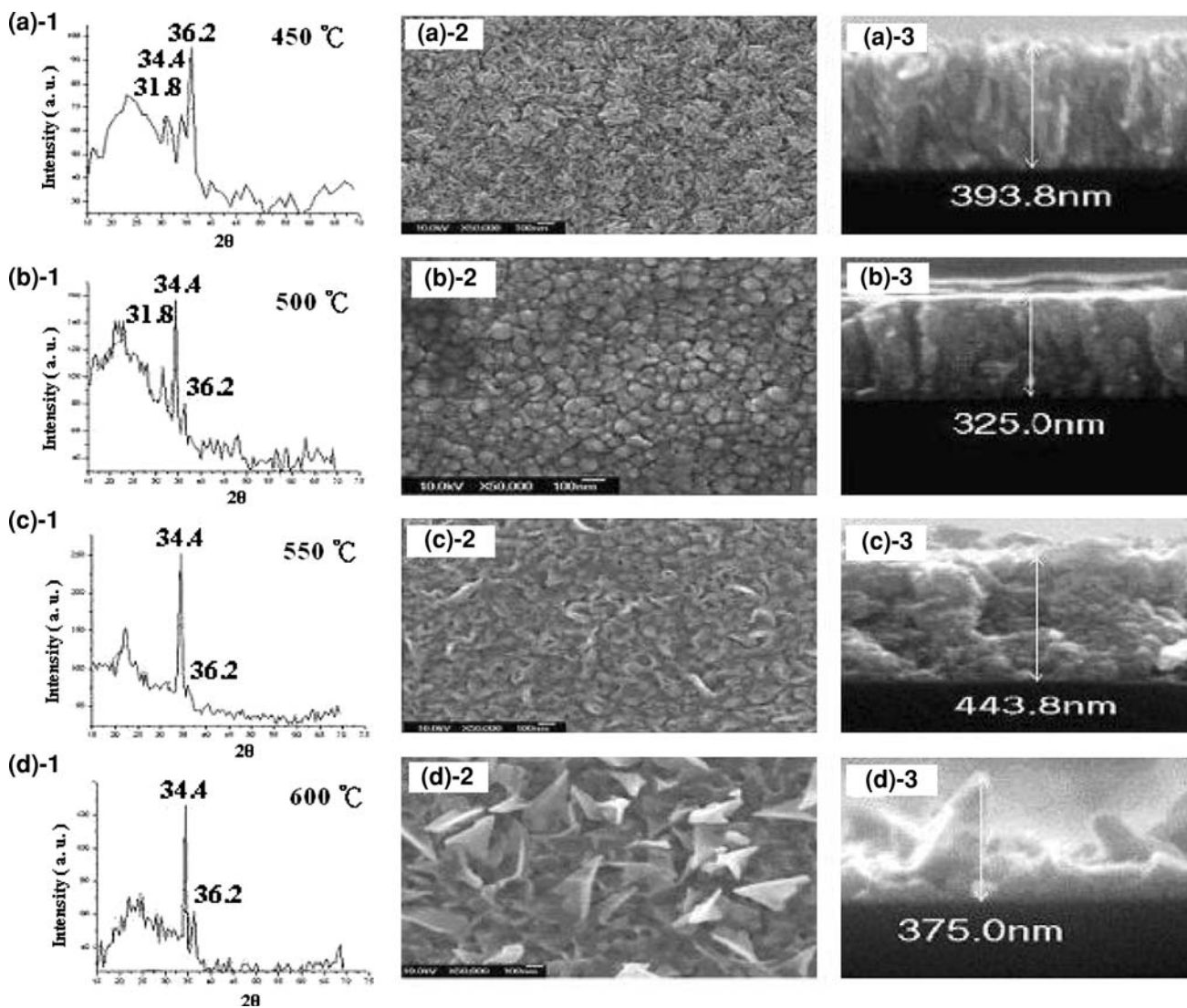
The substrates used in this study were cut from 2-inch (100)-oriented Si wafers. Prior to ZnO growth, the Si substrates were sequentially degreased in a mixture of vitriol and hydrogen peroxide, etched by a 10% HF solution for 2 min and then rinsed by deionized (DI) water. Undoped ZnO thin films were grown on Si (100) substrates by MOCVD system with a vertical reactor at atmospheric pressure. Diethylzinc (DEZn) and oxygen (O<sub>2</sub>) were used as the precursors for Zn and O, respectively, and nitrogen (N<sub>2</sub>) was employed as the carrier gas. The DEZn bubbler was kept at 20 °C in a glycol solution. Besides, the VI/II ratio was fixed at 66.86 by maintaining the flow rates of DEZn and O<sub>2</sub> at 16.7 and 1,116.1 μmol/min, respectively, during the growth. A 500 Å-thick ZnO nucleation layer deposited at 205 °C was used as the buffer layer. Top ZnO films were then deposited at temperatures varying from 450 to 600 °C for 40 min while the other deposition parameters, such as the flow ratio of DEZn and O<sub>2</sub> and carrier gas were remained the same as described above. The deposition rate of ZnO films, which is dependent on the deposition temperature, resultantly varied from 8.125 to 11.095 nm/min.

The crystalline quality of the samples was characterized by X-ray diffraction (XRD) using copper K $\alpha_1$  radiation as the detecting source. A scanning electron microscope (SEM) was employed to observe the surface morphology and cross-sectional images of ZnO films. Optical properties of ZnO thin films were examined by photoluminescence (PL) measurements carried out both at room temperature and in a temperature variant way from 20 to 300 K. A continuous-wave He–Cd laser operated at 325 nm was used as the excitation source. The excitation source has an output power of 55 mW and the excitation power density incident on the samples is about 1 W/cm<sup>2</sup>. A monochromator (Acton Research Corp. SP275) was used to disperse the PL emission from samples. The luminescence signal was detected by a photomultiplier tube (Hamamatsu R928) and triggered with a lock-in amplifier (Stanford Research Systems SR830). The ZnO sample was cooled down to 20 K using a closed-cycle helium refrigerator. The direct influence of He–Cd laser on the PL spectra of ZnO samples was prevented by using a polariscope to filter the laser signal.

## 3 Results and discussion

In general, the lattice mismatch between wurtzite ZnO and Si (100) substrate is about 67% [13], which causes a distortion in the lattice of the deposited ZnO thin films and brings in a large number of defects therein. The XRD spectra of ZnO films deposited at 450, 500, 550 and 600 °C are illustrated in Fig. 1a-1 to d-1, respectively. The diffraction peaks appearing at 31.8°, 34.4° and 36.2° correspond to the (10 $\bar{1}0$ ), (0002) and (10 $\bar{1}\bar{1}$ ) planes of wurtzite ZnO, respectively [11]. It exhibits that all ZnO grown films are polycrystalline. The morphology of the ZnO films deposited was also found to be greatly influenced by the deposition temperature. As demonstrated in Fig. 1a-2, grains with a sheet structure were observed on the surface of ZnO film grown at 450 °C. Otherwise, when the film was deposited at 500 °C, the structure of grains changed from sheets to lumps as can be seen from Fig. 1b-2. Note that all lump-shaped grains seemed to align along the *c*-axis of the wurtzite structure. However, when the film was deposited at 550 °C, as shown in Fig. 1c-2, the orientation of lump structure became ambiguous. At this moment all the grains seemed to be surrounded by various facets, which appeared probably because of the effect of growth anisotropism. Resultantly, all the grains in view exhibited an image of random alignments. Finally, when the deposition temperature was elevated to 600 °C, the growth was initiated by much more larger grains and therefore evidently three-dimensional (3D) microstructures without definite orientations appeared on the ZnO film surface, as can be found from Fig. 1d-2. The thickness of ZnO thin films was recognized by SEM observations, which was found to be dependent on the deposition temperature and resolved as 394, 325, 444 nm for the specimens fabricated at 450, 500, 550 °C, respectively. However, only an average thickness of 235 nm could be estimated for the film deposited at 600 °C. Obviously from the cross-sectional SEM images that the ZnO film grown at 500 °C is quite smooth in comparison with the film grown at 600 °C. This might suggest that the growth of ZnO thin films at low temperatures are much more easier to be conducted in a 2D mode compared with that carried out at 600 °C, however, further study is required to clarify this plausibility, such as a more detailed investigation on the initial stage of growth must be carried out.

Figure 2 shows the room temperature PL spectra obtained from ZnO films fabricated at different temperatures. Obviously, a dominant band peaking at a range from 3.27 to 3.29 eV can be found for all samples. This PL band is considered to be a combination of multiple luminescent mechanisms related to the free excitons and their phonon replicas based on what has been reported previously that only free excitonic emission can be observed at room

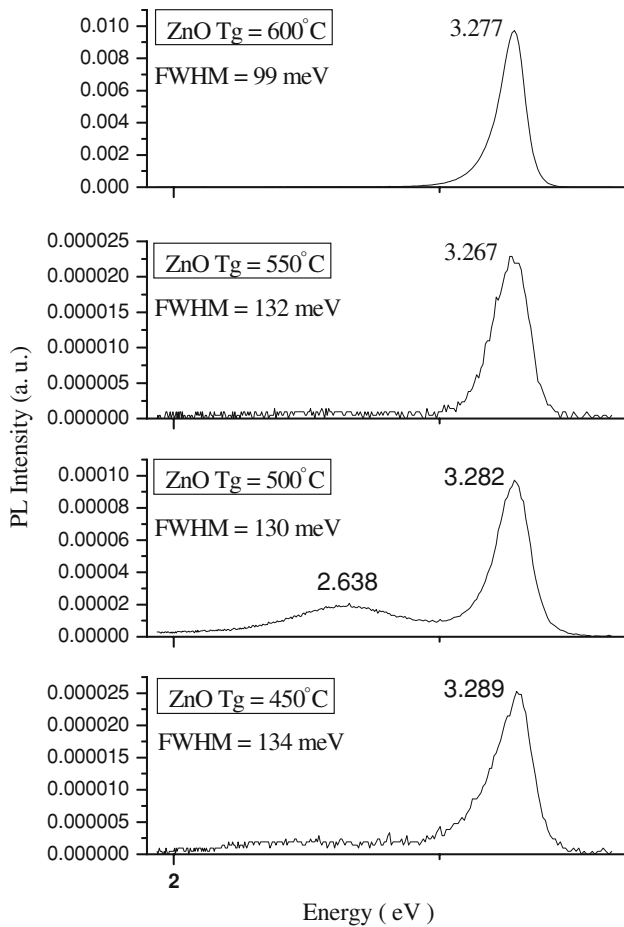


**Fig. 1** XRD spectra, surface and cross-sectional SEM images of ZnO films grown at different temperatures: (a) 450 °C, (b) 500 °C, (c) 550 °C and (d) 600 °C

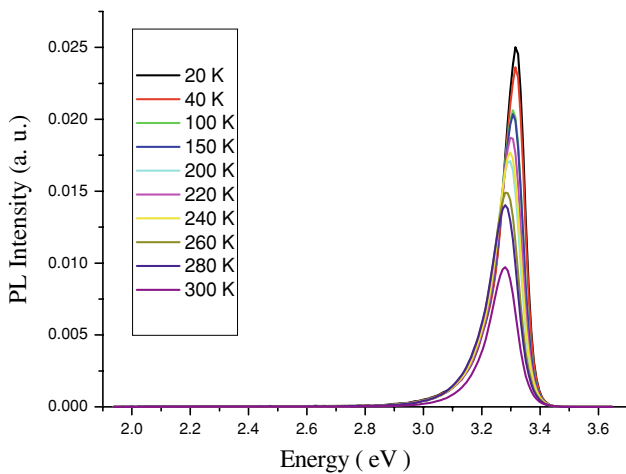
temperature [1, 14]. It should be noted that a smallest full-width at half-maximum of 99 meV was observed for the PL spectra from the film grown at 600 °C. In particular, a visible band peaking at 2.638 eV concerned with the deep-level emissions and present in other samples almost disappeared in the one fabricated at 600 °C. Low defect density and low impurity epitaxial ZnO thin films is evidenced by a reduction in the magnitude of the deep-level emission when compared to bulk material and CVD epilayers [12]. The typical intensity ratio of the near band edge emission to deep-level emissions is above 392 for the film fabricated at 600 °C and between 30 and 5 for the films fabricated at other temperatures. While, in the case of bulk material this ratio usually approaches zero as the temperature is raised to 295 K. Consequently, it seems to imply that the 3D microstructures formed in ZnO film

deposited at 600 °C help to improve the optical property of ZnO films. In the following, the PL spectra from the specimen fabricated at 600 °C are analyzed in more detail.

Figure 3 displays the temperature-dependent PL spectra measured at 20–300 K for the specimen fabricated at 600 °C. In commonly fabricated ZnO films and bulk crystals, free exciton emission is rarely observed at low temperatures because of the localization of excitons by impurities or defects, especially by donors. As can be seen from Fig. 3, no sharp peaks with a FWHM of several meV representing free or bound excitons can be definitely observed in the low temperature PL spectra. This is probably due to that the present undoped ZnO films show n-type conductivity with a high electron concentrations of about  $10^{19} \text{ cm}^{-3}$ , which has changed the band structure to some degree. The reason why the high carrier

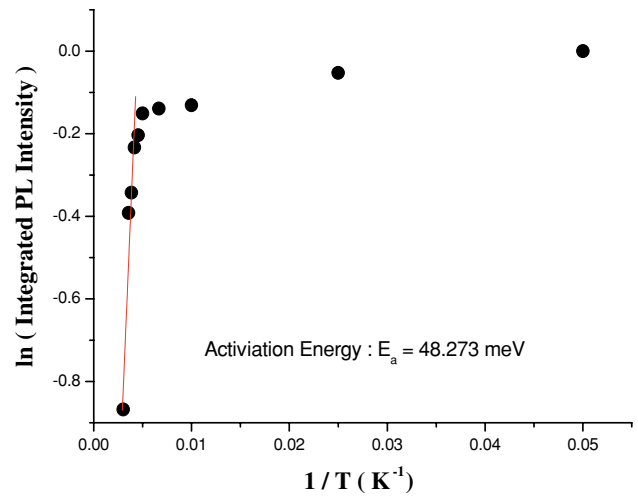


**Fig. 2** Room temperature PL spectra of ZnO thin films grown at different temperatures

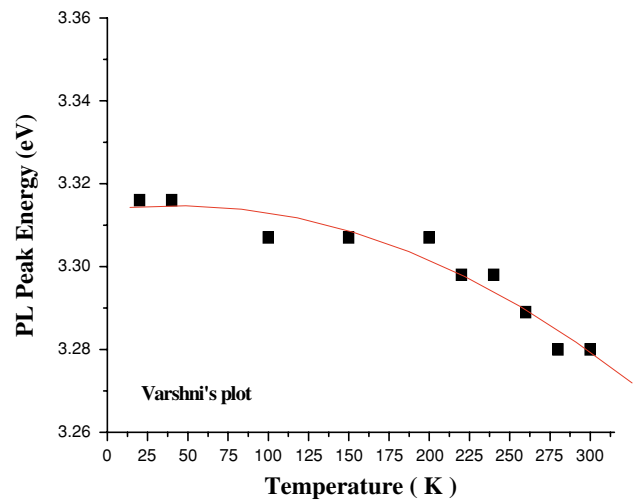


**Fig. 3** Temperature-dependent PL spectra of the ZnO films grown at 600 °C

concentration was achieved is still unclear now and the details involved are required to be further investigated. Both thermal quenching and red-shift behaviors can be



**Fig. 4** Variation of integrated PL intensity as a function of 1/T



**Fig. 5** Variation of the PL peak energy as a function of temperature for the ZnO film deposited at 600 °C

found from Fig. 3. Figure 4 plots the variation of integrated PL intensity as a function of the inverse of temperature for the sample mentioned in Fig. 3. From the data points in the high temperature range near room temperature one can evaluate the activation energy of 48.3 meV, which is believed to be the binding energy of donor bound exciton and in good agreement with what has been reported for the activation energy of the donors in ZnO, which is about 46–73 meV [15].

In addition, Fig. 5 shows the variation of PL peak energy as a function of measurement temperature for the same sample. The variation tendency can be well simulated by Varshni empirical equation [16] as follows.

$$E_g(T) = E_g(0) - \alpha T^2 / (T + \beta)$$

where  $E_g(T)$  is the band gap energy,  $T$  is temperature, and  $\alpha$  and  $\beta$  are fitting parameters.  $\alpha$  and  $\beta$  were found to be

$1 \times 10^{-4}$  eV/K and 700 K, respectively. This result presents another proof to explain the luminescent mechanism of the ZnO film fabricated at 600 °C is dominated by the free excitonic emission and the optical properties are recognized.

#### 4 Summary and conclusions

ZnO thin films were deposited on Si (100) substrate by atmospheric pressure metal-organic chemical vapor deposition at temperatures varying from 450 to 600 °C. X-ray diffraction analyses demonstrated all the films grown to be a wurtzite polycrystalline structure. Scanning electron microscopy observations indicated that the ZnO film grew with *c*-axis aligned grains when the deposition temperature was lower than 600 °C. However, when the film was deposited at 600 °C 3D microstructures without definite orientations were found. Room temperature PL spectra peaking at 3.27–3.29 eV were observed for the ZnO films grown at various temperatures. However, only the spectrum from the film grown at 600 °C could present a high intensity ratio of the near band edge emission to deep-level emissions, which is above 392 and show a minimum full-width at half-maximum of 99 meV. Temperature-dependent PL measurements from 20 to 300 K also exhibited the near band excitonic emission properties of the present ZnO films.

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