Structural and Luminescent Properties of ZnO Thin Films Deposited by Atmospheric Pressure Chemical Vapour Deposition *

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ZnO thin films were successfully deposited on Si (100) substrates by chemical vapour deposition (CVD) at atmospheric pressure (1 atm). The only solid source used here is zinc acetate, $(CH_3COO)_2Zn$, and the carrier gas is nitrogen. The sample, which was prepared at 550°C during growth and then annealed in air at 900°C, has only a ZnO (002) diffraction peak at 34.6° with its FWHM of 0.23° in the XRD pattern. The room-temperature PL spectrum shows a strong ultraviolet emission with the peak centred at 380 nm. We analysed the effects of many factors, such as the source, substrates, growth and annealing temperatures, and annealing ambience, on the structural and optical properties of our prepared ZnO films.

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With a wide direct band gap, the II-VI group semiconductor material ZnO thin film has many superior optical and electrical properties. At room temperature its band gap is 3.3 eV, which makes it a promising material for solar cells,[1] surface acoustic wave devices,[2] light emitting diodes,[3] and laser diodes.[4] Moreover, its exciton bonding energy is as large as 60 meV, 2.4 times that of GaN,[5] so it is a candidate for UV semiconductor materials of the next generation.

In recent years, many researchers reported that ZnO thin films can be grown by many methods, such as metal-organic chemical vapour deposition,[6] pulsed laser deposition,[7] dc sputtering,[8] molecular beam epitaxy,[9] spray pyrolysis [10], sol-gel process,[11] and so on. Chemical vapour deposition (CVD) [12] is a simple but useful method for preparing high quality films. It has many advantages such as high growth rate, large uniform area growth, and various thermodynamic parameters for control, etc. Many sources, such as diethylzinc (DEZn),[6] zinc acethylacetonate,[13] and zinc acetate (ZA),[12] have been used as precursors. In this study, our ZnO thin films with (002) orientation were prepared by CVD at atmospheric pressure using zinc acetate as a precursor, and we discuss the effect of different growth parameters on the crystal quality and luminescence properties of ZnO films.

The ZnO thin film samples were prepared on Si (100) substrates by atmospheric pressure CVD. Figure 1 shows the schematic of our CVD system. The precursor used here was solid zinc acetate (ZA). The carrier gas is nitrogen (N_2), flowing through a semi-enclosed quartz boat, which held the ZA source. Its flow rate was held from 0.5 L/min to 1.5 L/min by a gas flow controller. The ZA temperature was kept in the range 150–200°C. The Si substrate was put on a especially tilted quartz boat with temperature varying from 400°C to 600°C. The ZA was sublimated at low temperature and then was carried by N2 to the Si substrate, which was maintained at high temperature. Then it decomposed to form ZnO on the substrate surface. The x-ray diffraction (XRD) patterns of the samples were measured with a D/MAX-RA diffractometer, and the PL spectra were measured by a Hitachi 850 fluorescence spectrometer with the excitation wavelength of 210 nm.

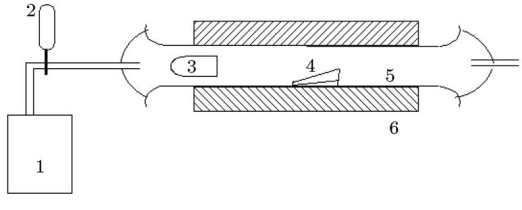


Fig. 1. Schematic of the CVD system: 1. high pure N_2 gas, 2. flow controller, 3. zinc acetate on a semi-enclosed quartz boat, 4. Si on a tilted quartz boat, 5. reaction quartz tube, 6. heating furnace.

The experimental results indicate that the crystal quality of the samples depends on the growth temperature, the flow rate of carrier gas and the annealing temperature. The luminescence properties are related to the growth and annealing ambience.

Firstly, we investigate the effect of different growth temperatures and different Si substrates. Figures 2(a)–(d) show the XRD patterns for the samples prepared on Si (100) at different growth temperatures of 400°C, 450°C, 470°C and 550°C, then annealed at

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900°C for all the samples. It is obvious that the orientation of the ZnO thin film can be improved with the increasing growth temperature. We suggest that higher temperature in our experiment conditions enables the reactant vapours to obtain enough kinetic energy to move and diffuse on the substrate surface until they find suitable growth points, hence to form better thin films.

Table 1. Growth conditions of all the samples.

Serial number	Substrate style	Source	Substrate temperature (°C)	Carrier gas/Flux (L/min)
a	p-Si (100)	$Zn(AC)_2$	400	N_2/1.5
b	p-Si(100)	$Zn(AC)_2$	450	N_2/1.5
c	p-Si(100)	$Zn(AC)_2$	520	N_2/1.5
d	p-Si(100)	$Zn(AC)_2$	550	N_2/1.5
e	p-Si(100)	$Zn(AC)_2$	500	N_2/0.8
f	p-Si(111)	$Zn(AC)_2$	500	N_2/0.8

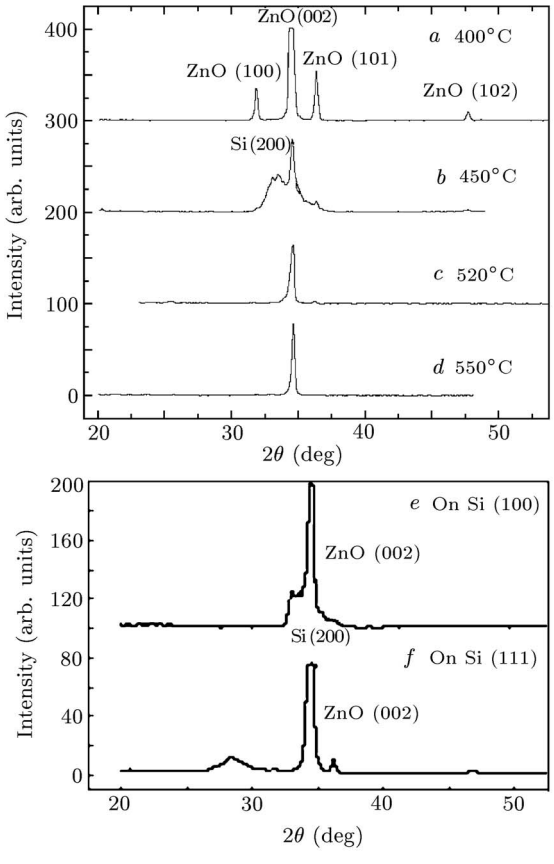


Fig. 2. XRD patterns of the samples grown at different temperatures (curves *a*–*d*) and grown on different crystal planes of the Si substrates (curves *e* and *f*).

We have also deposited ZnO thin films on different crystal planes of the substrates while keeping the other growth parameters unchanged. The results are shown in Figs. 2(e) and (f). It is found that the full width at half maximum (FWHM) of ZnO(002) peaks for the samples deposited on Si(100) is narrower than those of the samples deposited on Si(111). Besides the ZnO(002) peak, we could also find other diffraction peaks on the sample deposited on Si(111), such as ZnO(101), ZnO(102), and ZnO(103), etc. This result indicates that the orientation of the samples deposited on Si(100) is much better.

Secondly, we study the effect of different annealing temperatures. The XRD patterns of the ZnO thin films with different annealing temperatures are shown in Fig. 3. Curve *a* is for the unannealed sample. Curves *b* and *c* are for the sample annealed at 800°C and 900°C, respectively. From the comparison of these three XRD patterns, we can easily find that the crystal quality of the 900°C-annealed sample is better than that of the unannealed and the 800°C annealed ones. The 900°C-annealed sample has only a strong (002) diffraction peak at 34.6°, with the FWHM of 0.23°. Curve *d* is the rocking curve of the (002) peak in curve *c*. Obviously, it has a narrow protuberant peak between 17.184° and 17.450°, with the FWHM of about 1°. This result also indicates that the ZnO thin film has its single orientation along the *c*-axis.

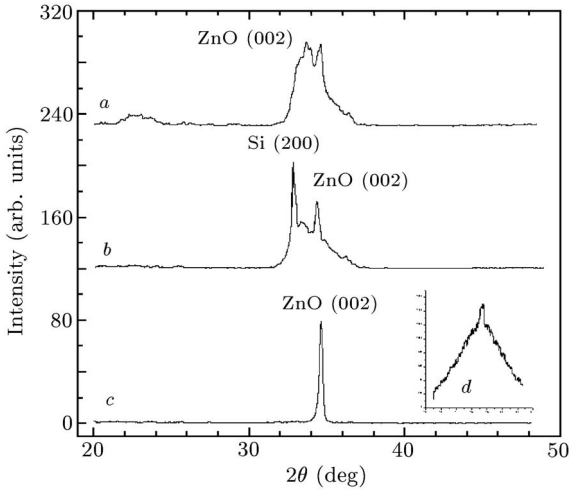


Fig. 3. XRD patterns of the samples grown at 550°C without annealed (*a*) and with different annealing temperatures (*b*) 800°C and (*c*) 900°C. (*d*) Rocking curve of the (002) peak (corresponding to curve *c*) with a narrow protuberant peak located between 17.184° and 17.450°.

Table 2. Annealing conditions of the samples.

Serial number	Substrate style	Source	Annealing temperature/time (°C/h)	Annealing ambience/flux (L/min)
a	p-Si(100)	$Zn(AC)_2$	900/1	N_2/0.5
b	p-Si(100)	$Zn(AC)_2$	900/1	O_2/0.7
c	p-Si(111)	$Zn(AC)_2$	900/1	N_2/0.5
d	p-Si(111)	$Zn(AC)_2$	900/1	O_2/0.7

Thirdly, we investigate the effect of the different annealing ambiences. The ZnO thin films were annealed in different ambiences while keeping the other parameters unchanged. The annealing conditions of the samples are listed in Table 2.

The room-temperature PL spectra of the samples were measured by a Hitachi 850 fluorescence spectrometer with the excitation wavelength of 210 nm, as shown in Fig. 4. We can see that the green peak of the ZnO thin films annealed in O_2 is much stronger than that of the samples annealed in N_2. Their intensity ratio is about 2:1–3:1. According to the above results and the green peak position,[16] we suggest that the green emission is mainly related to the defect O_{Zn}.

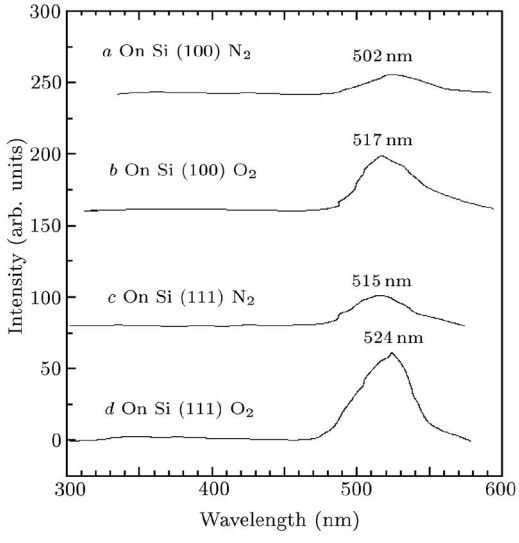


Fig. 4. Room-temperature PL spectra of the samples with the excitation wavelength of 210 nm.

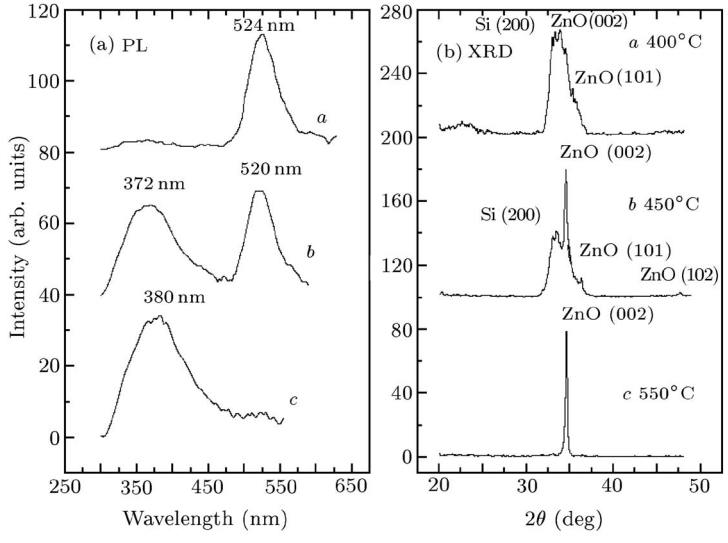


Fig. 5. (a) PL spectra and (b) XRD patterns of the samples grown at 400°C, 450°C, and 550°C. All of the samples were annealed at 900°C.

Fourthly, we study the relationship between the PL spectra and the XRD patterns. Figures 5(a) and (b) show the PL spectra and their corresponding XRD patterns of three samples *a*, *b* and *c*, which were grown at different temperatures but annealed at the same temperature. In the PL spectra, we can see that curve *a* only has a green peak centred at 524 nm; curve *b* has green and ultraviolet peaks at 520 nm and 372 nm, respectively, almost with the same intensity; and curve *c* only has an ultraviolet peak at 380 nm. From the corresponding XRD patterns, we conclude that the luminescence peak of the ZnO thin films changes from green to ultraviolet with the improvement of the ZnO(002) orientation. According to previous researchers, the green peak is caused by some defects such as V_O, Zn_i, and O_{Zn}, etc.[14–16] These defects will be decreased, if the quality of ZnO films improves, so that the green peak is consequently decreased or even disappears. Meanwhile, the ultraviolet peak, which is mainly caused by free-exciton recombination, increases.

In summary, we have deposited ZnO thin films on Si substrates by a novel simple CVD method, in which the only source used is zinc acetate, $(CH_3COO)_2Zn$. We find that the crystal structures and the PL spectra of the samples strongly rely on the growing and annealing conditions. The sample which was grown at 550°C and then annealed in air at 900°C only has a (002) peak at 34.6° with the FWHM of 0.23° in its XRD pattern. The FWHM of 1° on the rocking curve of the (002) orientation shows the perfect crystalline quality of our sample. Also, the only ultraviolet emission peak observed in the PL spectra is at 380 nm.

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