ORIGINAL RESEARCH PAPER

Effect of growth time on ZnO thin films prepared by low-temperature chemical bath deposition on PS substrate

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ABSTRACT
ZnO thin films were successfully synthesized on a porous silicon (PS) substrate by chemical bath deposition method. X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), and photoluminescence (PL) analyses were carried out to investigate the effect of growth duration (3, 4, 5, and 6 h) on the optical and structural properties of the aligned ZnO nanorods. The small FWHM and stronger diffraction intensity of growth times of 5 h mean the better crystal quality of ZnO thin films compared to others. The grain size of the ZnO thin films gradually increased with increased the growth time. The FESEM images show that the thickness of ZnO thin films increased with increase of the growth time. Photoluminescence measurements showed that there was a sharp and highly intense UV emission peak when growth time was 5 h. The structural and optical investigations revealed that the ZnO thin films grown on the PS substrate with growth time of 5 h had high structural and optical quality.

Keywords: *Chemical Bath Deposition; Crystal Structure; Growth Time; Porous Silicon; ZnO Thin Films*

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INTRODUCTION

ZnO thin films are intrinsically n-type semiconductors with a wide direct band gap of 3.37 eV and a large exciton binding energy of 60 meV; they possess unique optical, high mechanical and thermal stabilities, and electronic properties. ZnO thin films have drawn much attention in the last decade because of their potential applications in optoelectronic and electronic devices, such as light emitting diodes [1], gases sensors [2], acoustic devices [3], UV photodetectors [4], and solar cells [5]. A number of deposition techniques such as molecular beam epitaxy (MBE) [6], radio frequency sputtering [7], atomic layer deposition (ALD) [8], pulsed laser deposition (PLD) [9], chemical vapor deposition (CVD) [10] have been used to produce ZnO thin films. ZnO nanostructures grown on Si-based substrates have been attracted significant interests in the past few decades because silicon substrate is a stable and high temperature resistant material and a very popular substrate in IC technology [11, 12]. However, it is difficult to directly grow or deposit high quality ZnO nanostructures on silicon substrates, because there is a large stress between ZnO and Si substrate due to the mismatch in their thermal expansion coefficients and lattice constants [13]. Therefore, it is necessary to look for a better substrate for growing high quality ZnO nanostructure. Among various porous semiconductors, the porous silicon (PS) substrate has recently drawn much attention for its application in the development of silicon-

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based optoelectronic devices because of its strong absorbability, large internal surface, adjustable roughness, high resistance, and low cost. Moreover, PS prepared by the silicon is compatible with silicon IC technology, which provides a possibility to integrate PS-based optical devices [14]. The porous silicon layer reduces the large mismatches in the lattice constants and thermal expansion coefficients between the ZnO and Si substrates, which also reduces the large stress between the ZnO nanostructures and Si substrate [15]. So far, the ZnO thin films have been widely fabricated by numerous techniques [16-20] but chemical bath deposition (CBD) technique is one of the appropriate chemical synthesis to produce ZnO thin films on various substrates because of its low temperature, non-requirement of sophisticated instruments, simplicity, capability for large-scale production, and affordability. It has been known that the growth time used for chemical bath deposition synthesis affect the formation of the ZnO thin films. A detailed understanding of structural and optical properties of ZnO thin films is essential for use of ZnO thin films in the optoelectronics industry because of the carrier relaxation processes strongly affect optoelectronic and electronic characteristics of ZnO thin films. However, few systematic studies have been considered the effect of the growth duration on both the structural and optical properties of ZnO thin films grown by chemical bath deposition technique, especially using PS substrates. To the best of my knowledge, this research is the first to examine the effect of growth duration on the structural and optical properties of seed layer-free ZnO thin films synthesized on PS substrate by CBD technique. Furthermore, in this research, the XRD, FESEM, and PL spectroscopy utilized to study the effect of growth times on the structural and optical properties of fabricated ZnO thin films on PS substrates.

EXPERIMENTAL

ZnO thin films were prepared on PS substrate by the chemical bath deposition technique. There are several major steps in this experiment, which are the preparation of the PS substrate and the solution, deposition process and characterization process. The porous structure was formed on a n-type Si (100) substrate using the photo electrochemical etching method. The photo electrochemical etching process was carried out in a Teflon cell containing a mixture of hydrofluoric acid and 96% ethanol with a volume ratio of 1:4. The PS layer was formed with a constant current density of 20 mA/cm^2 for 5 min at room temperature using the Pt wire and Si as cathode and anode, respectively. The sample was illuminated with a 60 W visible lamp during the etching process. The prepared PS substrates were rinsed deionized (DI) water and dried with nitrogen gas [21]. A 0.050 M/L of zinc nitrate hexahydrate $Zn(NO_3)_2.6H_2O$ and an equal molar concentration of hexamethylenetetramine $C_6H_{12}N_4$ were dissolved in DI water at 80 °C separately. The two solutions were combined and the samples were vertically placed in a beaker. To study the influence of growth duration, the beaker was placed in an oven for various durations (3, 4, 5, and 6 h) at 90 °C to grow ZnO thin films. Then, the samples were rinsed with DI water and were dried with nitrogen (N_2) gas.

The crystal structure of the ZnO thin films was obtained using X-ray diffraction (XRD) (PANalytical X'Pert PRO MRD PW3040). The surface morphology of ZnO thin films was investigated by using field emission scanning electron microscopy (FESEM) (model FEI/ Nova NanoSEM 450). Photoluminescence (PL) spectroscopy (Jobin Yvon HR 800 UV, Edison, NJ, USA) was used to characterize the optical properties of the ZnO thin films at room temperature.

RESULTS AND DISCUSSION

Fig. 1 (a) shows XRD patterns of ZnO thin films grown on Si and PS substrates. The XRD patterns of ZnO thin films with different growth times are shown in Fig. 1 (b). For all the ZnO thin films, a strong diffraction peak (0 0 2) with polycrystalline hexagonal wurtzite crystal structure (The standard data for ZnO; ICSD 01-074-0534) are only observed, indicating that the preferred orientation due to the low surface free energy is along the c-axis perpendicular to PS substrates [22]. As shown in Fig. 1(a), a higher intensity and a narrower FWHM of the (002) diffraction peak demonstrate that the ZnO thin film grown on PS substrate compared with Si substrate has good crystallinity. These results insinuate that the PS had some impact on enhancing the crystal quality of the ZnO thin films. The XRD peak position, full width at half maximum (FWHM), lattice constant (c), stress, grain size, and degree of orientation of the ZnO (002) planes for ZnO thin films grown on Si substrate and PS substrates with different growth times are summarized in Table 1. The (0

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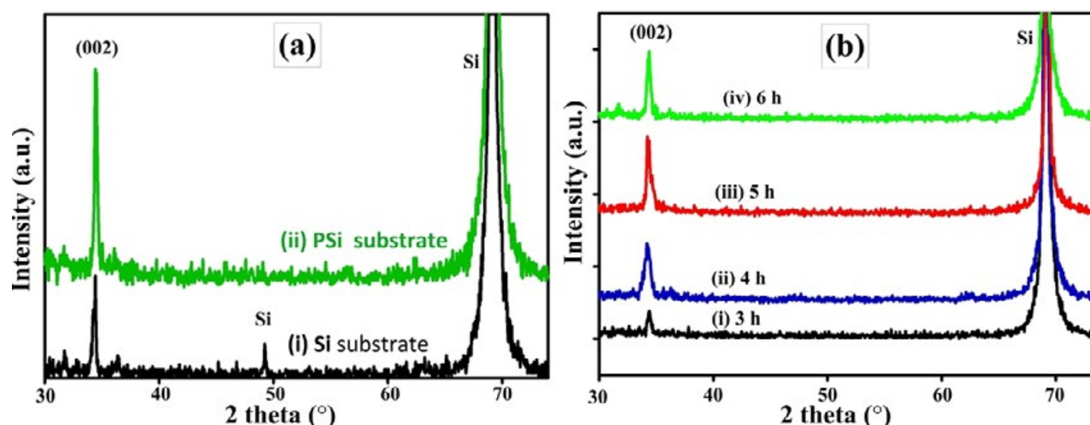

Fig. 1. (a) Typical XRD patterns of ZnO thin films grown on Si and PS substrates at 95 °C for 5 h, (b) XRD patterns of ZnO thin films grown on PS substrate with different growth times at growth temperature of 90 °C.

Table 1. Summarized data from XRD patterns of ZnO thin films grown on Si substrate and PS substrates with different growth times.

ZnO thin film	growth time (h)	(002) peak position (°)	FWHM of (0 0 2) peak	c (Å)	Stress (GPa)	Grain size (nm)	Degree of (002) orientation
Si substrate	5	34.275	0.48	5.2279	-0.871	34.63	0.472
PS substrate	3	34.175	0.53	5.2427	-1.48	31.36	0.485
PS substrate	4	34.175	0.50	5.2427	-1.48	33.24	0.680
PS substrate	5	34.225	0.44	5.2353	-1.18	37.78	0.721
PS substrate	6	34.275	0.43	5.2279	-0.87	38.66	0.563

0 2) peak position of ZnO thin film shifts to the higher 2θ angles from 34.175 ° to 34.275° with increased the growth times. The lattice constant (c) of (0 0 2) peak of ZnO thin films decreased as the growth times increased, as shown in Table 1. The diffraction intensity, obviously increases with the growth times and reaches to the maximum at 5 h, after that it decreased at 6 h. The small FWHM and stronger diffraction intensity of growth times of 5 h mean the better crystal quality of ZnO thin films compared to others.

The total stress of ZnO thin film originates from extrinsic and intrinsic stresses. The extrinsic stress is mainly associated with thermal expansion coefficient mismatch and lattice mismatch between the ZnO thin film and substrate, while the intrinsic stress is related to defects and impurities. XRD is often used to calculate the residual stress of ZnO thin films compared with other methods (such as Raman, and the technique of curvature measurement) because the strain can be calculated directly by using Bragg's equation. The residual stress σ in the plane of ZnO thin films with different growth times can be determined using the following expression [23, 24]:

$$\sigma = \frac{2C_{13}^2 - C_{33}\left(C_{11} + C_{12}\right)}{2C_{13}} \times \frac{c - c_0}{c_0} \qquad (1)$$

Where c is the lattice constants of the ZnO thin films obtained from the XRD data, c_0 (5.2066 Å) is the standard lattice constant for unstrained ZnO (ICSD 01-074-0534), and C_{ij} are the elastic stiffness constants of ZnO, i.e., C_{11} = 207.0 GPa, C_{33} = 209.5 GPa, C_{12} = 117.7 GPa and C_{13} = 106.1 GPa. The calculated stress of ZnO thin films with different growth times are given in Table 1. The negative sign of stress indicate the stress is compressive. The compressive residual stress of ZnO thin films decreased with increasing growth.

The degree of orientation of the (002) plane of the ZnO thin films for all samples were calculated using the following Lotgering relation of [25]:

$$F(hkl) = \frac{P(hkl) - P_0(hkl)}{1 - P_0(hkl)} \qquad (2)$$

Where $F(hkl)$ is the degree of (hkl) orientation, $P(hkl) = I(hkl)/\sum I(hkl)$ and $P_0(hkl) = I_0(hkl)/\sum I_0(hkl)$. Here $I(hkl)$ is the (hkl) peak intensity and $\sum I(hkl)$ is the sum of the intensities of all peaks in the ZnO thin films' diffraction data. $I_0(hkl)$ is the (hkl) peak intensity and $\sum I_0(hkl)$ is the sum of the intensities of diffraction peaks in the reference data (ICSD 01-074-0534). The calculated values of orientation degree of the (002) plane for all samples is given in Table 1.

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The grain size of the ZnO thin films along the (002) peak is obtained by the following Scherrer equation [26]:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (3)$$

Where D, θ, λ, and β represent the average crystallite size, Bragg diffraction angle, X-ray radiation wavelength, and FWHM value, respectively. The calculated grain size for all samples is given in Table 1. The grain size of the ZnO thin films gradually increased from 31.36 nm to 38.66 nm with increased the growth time of 6 h.

Fig. 2 illustrates FESEM images of ZnO thin films grown on (a) Si and (b) PS substrates at 95 °C for 5 h. FESEM images demonstrated that the thickness of ZnO thin film grown on PS substrate is more than Si substrate.

Fig. 3 shows the three-dimensional view and surface FESEM images of the ZnO thin films on PS substrate with different growth times: (a) 3 h, (b) 4 h, (c) 5 h, and (d) 6 h. Furthermore, the images show that the ZnO thin films were grown on the entire substrate surface. FESEM images demonstrate that most ZnO thin film structure is composed of columnar-structured grains. The average thickness of ZnO thin films grown on PS substrates increased from 145 nm to 330 nm with increased growth durations from 3 h to 6 h, respectively. As shown in Fig. 3, the thickness of fabricated ZnO thin films increased with increase of the growth times. The surface FESEM images show that the ZnO thin films fabricated with growth time of 5 h has a better surface morphology and bigger grain size compared with other samples.

The measurement of the photoluminescence (PL) spectra is an effective method of characterizing the optical properties and defects of ZnO thin

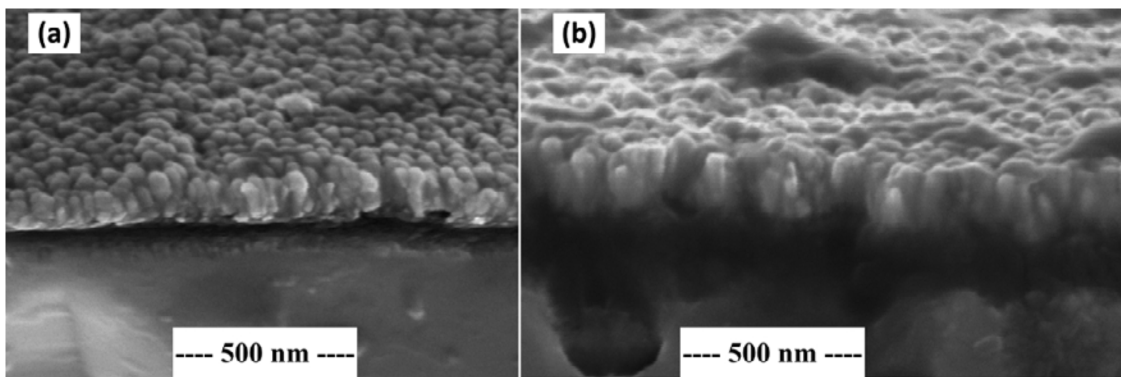

Fig. 2. Three-dimensional view FESEM images of ZnO thin films grown on (a) Si and (b) PS substrates at 95 °C for 5 h.

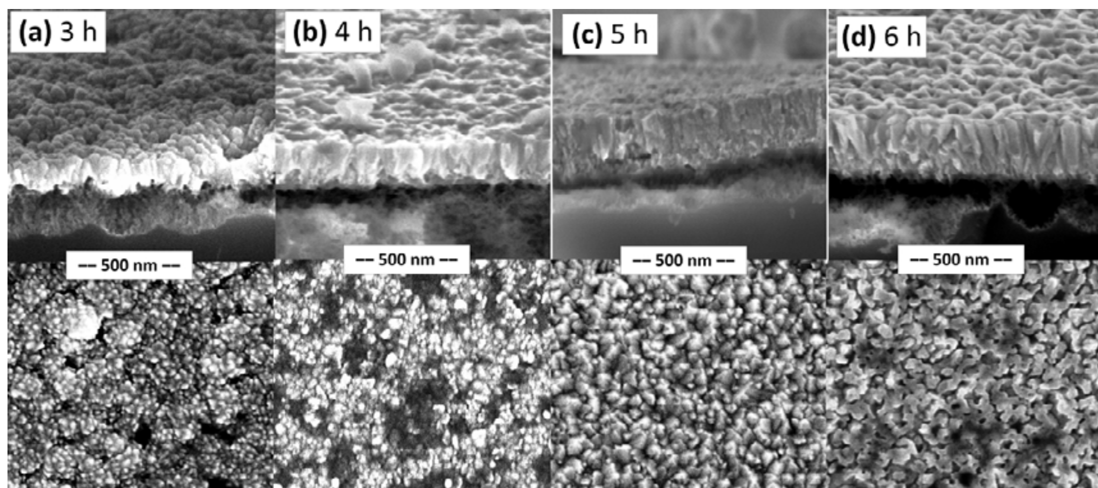

Fig. 3. Three-dimensional view and surface FESEM images of the ZnO thin films grown on PS substrate at 90 °C with different growth times: (a) 3 h, (b) 4 h, (c) 5 h, and (d) 6 h.

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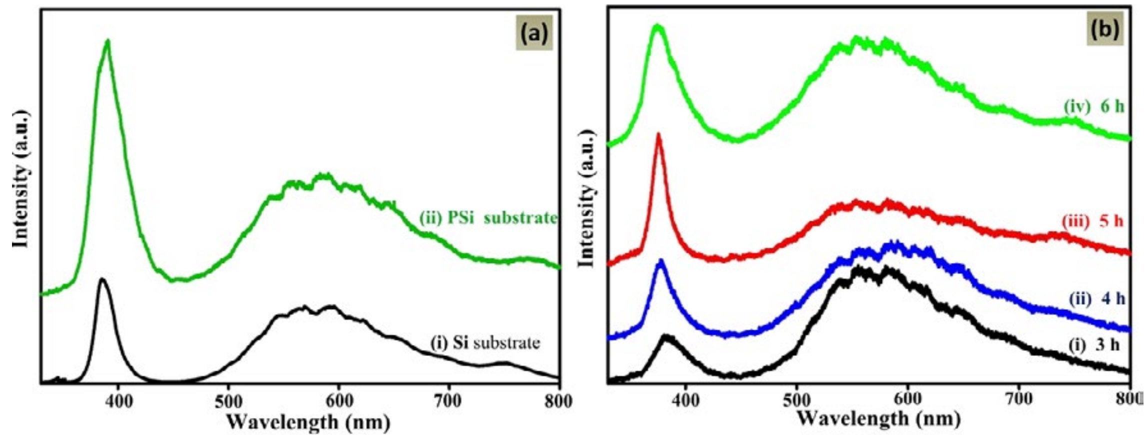

Fig. 4. PL spectra of ZnO thin films grown on Si and PS substrates at 95 °C for 5 h, (b) PL spectra of ZnO thin films grown on PS substrate at 90 °C with different growth times.

Table 2. Summarized data from PL spectra of ZnO thin films with different growth times.

Growth times	UV peak (nm)	FWHM of UV peak (nm)	I_{UV}/I_{DLE}
3	389	51.2	0.46
4	387	33.2	0.78
5	385	25.1	1.89
6	384	35.2	1.12

films. Fig. 4 (a) revealed the PL spectra of the ZnO thin films on Si and PS substrates with the growth time and temperature of 5 h and 95 °C, respectively. The intensity of the UV emission of the ZnO thin film grown on PS substrate was much higher than that of the ZnO thin film grown on Si substrate. The PL spectra of the ZnO thin films grown on PS substrates with different growth times of (i) 3 h, (ii) 4 h, (iii) 5 h, and (iv) 6 h are shown in Fig. 4 (b). The UV emission was attributed to the recombination of electron–hole in the near band edge energy levels and the visible emission that resulting from structural and intrinsic defects in ZnO such as oxygen and zinc vacancies, as well as oxygen and zinc interstitials in ZnO thin films was related to the deep-level emission of the ZnO band gap [27]. As shown in Fig. 5 (b), the intensity of the UV emission increased as the growth times increased to 5 h, but subsequently decreased at 6 h. It is known that the intensity ratio of UV emission (I_{UV}) to deep level emission (I_{DLE}) is a suitable approach to estimate the optical quality of ZnO thin films [28]. The calculated relative integrated PL intensity ratio (I_{UV}/I_{DLE}) for ZnO thin films grown on PS substrate with different growth times are given in Table 2. As shown in the Table 2, the intensity ratio (I_{UV}/I_{DLE}) increased as the growth time increases to 5 h, and then decreases when the growth time further increases up to 6 h. Generally, a relatively low value of the intensity ratio (I_{UV}/I_{DLE}) of the ZnO thin films fabricated by using chemical bath deposition method as compared to other deposition method can be related to larger number of defect sites, such as point defects, and non-stoichiometry [29]. Table 2 showed that the FWHM of UV peak decreased as the growth times increased to 5 h and then increased to 6 h. This finding indicates that the optical and crystallographic properties of the ZnO thin films were improved with growth time 5 h.

CONCLUSIONS

Seed layer-free ZnO thin films were successfully synthesized by using chemical bath deposition method on PS substrates with different growth times. XRD results showed that the ZnO thin films grown for 5 h had better structural quality and smaller tensile strain than those synthesized for other growth durations. The surface FESEM images show that the ZnO thin films fabricated with growth time of 5 h has a better surface morphology and bigger grain size compared with other samples. The intensity ratio (I_{UV}/I_{DLE}) of the ZnO thin films increased from 0.46 to 1.89 when the growth time was increased to 5 h. It was suggested that the growth time of 5h was the most suitable to obtain the high-quality ZnO thin films

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on PS grown by chemical bath deposition method. Therefore, growth duration considerably influenced the optical properties, structural properties, and growth of ZnO thin films.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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