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Feasibility of ZnO and Zn Seed Layers for Growth of Vertically Aligned and High-Quality ZnO Nanorods by the Sonochemical Method

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Abstract. The distinct roles of zinc oxide (ZnO) and zinc (Zn) seed layers in the growth of vertically aligned high-quality zinc oxide (ZnO) nanorods by the sonochemical method were investigated. ZnO nanorods were grown on p-type Si (111) with {Ti (10 nm)/ZnO (85 nm)}, {ZnO (85 nm)}, {Ti (10 nm)/Zn (55 nm)} and {Zn (55 nm)}. Ti (10 nm) was incorporated as the buffer layer. All depositions were carried out using RF-sputtering. The effects of the seed layers on the growth of vertically aligned high-quality ZnO nanorods (NRs) were systematically studied using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), energy dispersive X-ray (EDX) analysis and transmission electron microscopy (TEM). The results indicated that the ZnO nanorods synthesized using ZnO (85 nm) as seed layer, with and without the Ti buffer layer, have better average aspect ratio than those synthesized using Zn (55 nm) as seed layer. Therefore, ZnO serves as a potential and preferable seed layer for the synthesis of vertically aligned high-quality ZnO nanorods with lower compressive strains. Furthermore, the lattice mismatch between ZnO nanorods, seed layer and Si substrates was reduced with the introduction of thin Ti (10 nm) as a buffer layer. In general, the type and thickness of seed layer are key parameters to synthesize high quality ZnO nanorods.

Introduction

Zinc Oxide (ZnO) has drawn the attention of the scientific community due to its intrinsic advantages, which include wide direct band gap of 3.37 eV, large exciton binding energy of 60 meV, physical and chemical stability [1, 2], strong piezoelectricity [3] and non-toxic nature. Hence, ZnO is a potential and viable precursor material for the synthesis of nanorods. Over the years, ZnO nanorods have been utilized in UV detectors, gas sensing, chemical sensors, solar cells [4, 5], light emitting diodes (LEDs) and field - effect transistors [6]. In addition, uncoated ZnO has been used for many biomedical applications because it is biocompatible and bio-safe [7]. As such, an improvement in the growth parameters of the ZnO nanorods are required because it can lead to an enhancement in its applications.

The thickness and type of a seed layer are two of the most important parameters that significantly influence the morphology and structural properties of ZnO nanorods (diameter, length, and verticality) [8, 9]. Substrate properties is also important for the growth of high-quality ZnO nanorods. The Si substrate is the most preferred because of its diverse and distinctive properties, which include good thermal conductivity, high crystallinity, synthesizable large sizes and cost effectiveness [10,11,12]. In addition, the hexagonal surface of the ZnO (002) with unit cell of 3.25 Å closely matches the hexagonal surface of the Si substrate formed by the surface of six Si (111) triangle with a unit cell of 3.82 Å [13].

Several techniques have been utilized to synthesize ZnO nanorods. Based on the kind of reactions they undergo; these techniques can be broadly classified into: vapour-phase reactions and hydrothermal reactions. The vapour phase techniques can produce well aligned, homogeneously distributed and high crystalline ZnO nanorods [8]. However, the complexity of the process, high temperature and sophisticated equipment required make the techniques unattractive. On the other hand, nanostructures synthesized based on hydrothermal reaction are fraught with the challenge of the long reaction time required for the growth of ZnO nanostructures [14].

Alternatively, the sonochemical method can be used to rapidly and effectively grow vertically aligned ZnO nanorods on different substrates [14], without the drawbacks of the vapour-phase and hydrothermal methods. In this method, the high frequency ultrasound waves produced by the sonicator initiates acoustic cavitation in the liquid medium, which results in the generation of concentrated hotspot with extremely high temperature (5000 K) and pressure (1000 atm). The resultant chemical and physical effects produce various types of nanostructures [4, 15]. However, few number of researchers have reported the use of the sonochemical method for the synthesis of ZnO nanorods on various substrates [16], this is the first time the growth of ZnO nanorods by sonochemical method using ZnO as a seed layer on Si substrate via RF-sputtering has been performed. In this present work, the growth of vertically aligned high-quality ZnO nanorods were successfully produced using the following combination of thin films {ZnO (85 nm) / Ti (10 nm)/ Si}, {ZnO (85 nm)/Si}, {Zn (55 nm) / Ti (10 nm)/Si}, and {Zn (55 nm)/Si}.

Experiment

As shown in Table 1, the substrates of p-type Si (111) were divided into two groups after cleaning using the Radio Corporation of America method.

Table 1 Description of Samples.

Group	Sample	Buffer Layer [nm]	Seed Layer [nm]
I	A	Ti (10)	ZnO (85)
	B	-	ZnO (85)
II	C	Ti (10)	Zn (55)
	D	-	Zn (55)

As presented in Table 1, the buffer and seed layers of all samples were deposited by RF-sputtering. Aqueous solutions (100 mL) of zincnitrate hexahydrate ($Zn (NO3)_2.6H_2O$, 98%, Aldrich) and hexamethylenetetramine (HMT, $(CH2)_6N_4$, 99%, Aldrich) with similar concentrations of 0.05 M was stirred for 1.5 hours at room temperature to ensure proper mixing. ZnO nanorods were then grown by immersing the sample in the aqueous solution, which was subsequently sonicated using the ultrasonic probe at amplitude of 40% for 2 hours. The resulting samples were carefully washed with deionised water and dried in an oven at 150 °C for 5 minutes

Characterization. The morphology of the ZnO nanorods arrays was analyzed using field emission scanning electron microscope (Model JSM- 6460LV), while their elemental composition was studied using energy dispersive X-ray analysis attached to the FESEM. The energy-filtered transmission electron microscopy (EFTEM) was utilized for the characterization of nanorods at atomic level (model Philips / FE1 CM12). The structure and growth orientation of the ZnO nanorods were examined using X-ray diffraction (Panalytical X'pert Pro MRD PW3040).

Result and Discussion

The FESEM images of ZnO nanorods synthesized on p-type Si (111) substrate with (A) {Ti (10 nm)/ZnO (85 nm)}, (B) {ZnO (85 nm)}, (C) {Ti (10 nm)/Zn (55 nm)} and (D) {Zn (55 nm)} are shown in Fig. 1. From the top view of the ZnO nanorods, all samples display hexagonal crystal structure. The average diameters were ~54.2 nm, ~55.28 nm, ~55.4 nm and ~56.24 nm, for samples

A, B, C and D, respectively. The average length for samples A and B were ~ 670 nm, while for samples C and D were ~ 650 nm. The average aspect ratios of the ZnO nanorods were derived from the FESEM images using an earlier reported relation of average length divided by average diameter [17,18]. The average aspect ratios are 12.36, 12.12, 11.73 and 11.55 for ZnO nanorods grown using samples A, B, C and D, respectively. The average aspect ratio of the ZnO nanorods grown on ZnO seed layer (85 nm) with and without Ti (10 nm) is greater than those grown using Zn (55 nm) with and without Ti (10 nm). This indicates that ZnO nanorods grown on ZnO seed layer (85nm) will improve the performance of the nanodevices for any given application.

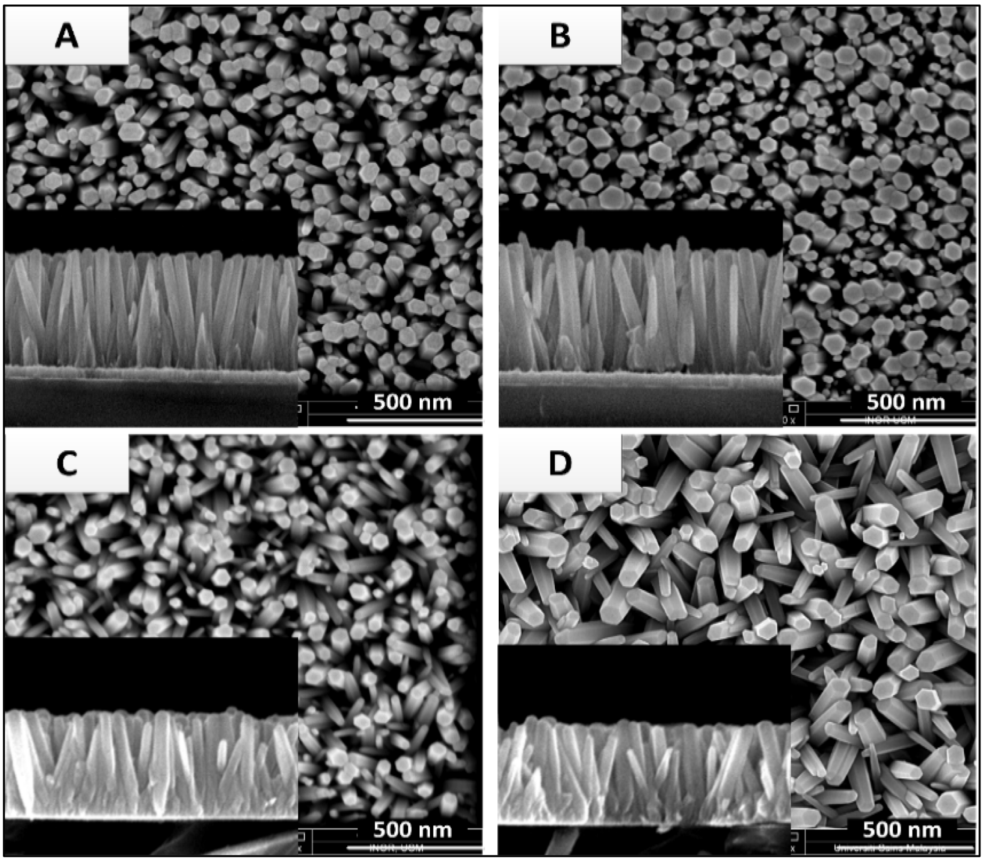
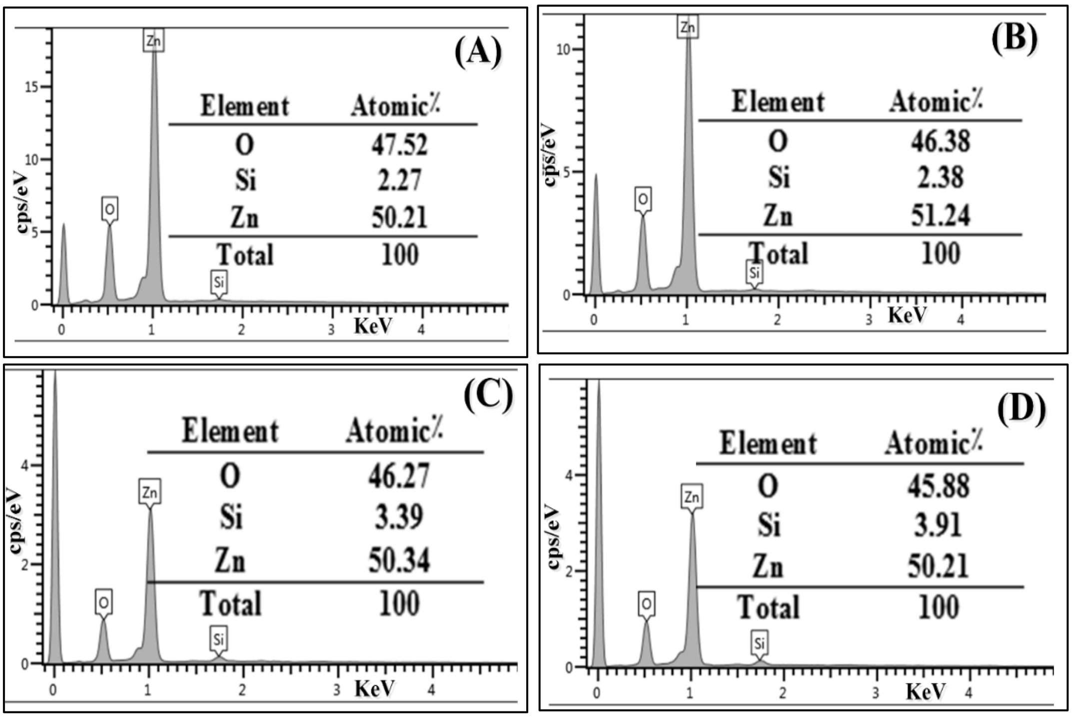


Fig. 1 SEM photographs of ZnO nanorods grown on p-type Si (111) with (A) {Ti (10 nm)/ZnO (85 nm)}, (B) {ZnO (85 nm)}, (C) {Ti (10 nm)/Zn (55 nm)} and (D) {Zn (55 nm)}.

The EDX analysis in Fig. 2 (A- D) revealed that when (A) {Ti (10nm) / ZnO (85nm)}, (B) {ZnO (85nm)}, (C) {Ti (10nm)/ Zn (55nm)} and (D) {Zn (55nm)} were used to synthesize ZnO NRs on Si substrate, only three elements can be found in the samples, which are zinc (Zn), oxygen (O) and silicon (Si). The Si element is from the silicon substrate. This result confirms the purity of ZnO phases synthesized using the sonochemical method.

The EFTEM images shown in Fig. 3 (A-D) confirm the hexagonal wurtzite structures of the ZnO nanorods. The ZnO nanorods synthesized from all samples are smooth, while the length of the ZnO nanorods synthesized from samples A and B are longer than those synthesized from samples C and D. The lengthier ZnO nanorods synthesized from samples A and B compared to C and D can be attributed to the different structural morphologies of ZnO (85 nm) and Zn (55 nm) seed layers, as well as the relatively lower activation energy and lattice mismatch between ZnO nanorods, seed layer and Si substrate or Ti / Si substrate in samples A and B [19]. Moreover, the seed orientation of ZnO (85 nm) strengthened the synthesized ZnO NRs along the c-axis [8]. Therefore, the average aspect ratio of ZnO nanorods is closely dependent on the thickness and type of seed layer.



(A)

Element	Atomic%
O	47.52
Si	2.27
Zn	50.21
Total	100

(B)

Element	Atomic%
O	46.38
Si	2.38
Zn	51.24
Total	100

(C)

Element	Atomic%
O	46.27
Si	3.39
Zn	50.34
Total	100

(D)

Element	Atomic%
O	45.88
Si	3.91
Zn	50.21
Total	100

Fig. 2 EDX analysis of ZnO nanorods grown on p-type Si (111) with (A) {Ti (10nm)/ZnO (85nm)}, (B) {ZnO (85nm)}, (C) {Ti (10nm)/Zn (55nm)} and (D) {Zn (55nm)}.

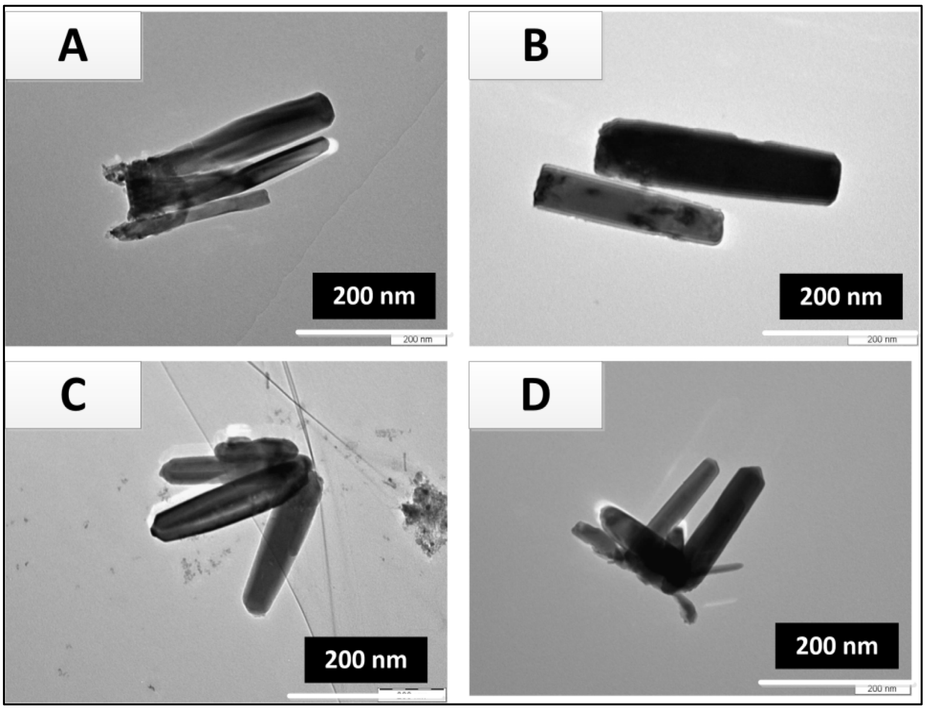


Fig. 3 EFTEM image of single ZnO nanorods grown on p-type Si (111) with (A) {Ti (10nm) / ZnO (85nm)}, (B) {ZnO (85nm)}, (C) {Ti (10nm)/ Zn (55nm)} and (D) {Zn (55nm)}.

Based on the XRD pattern in Fig. 4 (A- D), the (002) reflection peak clearly has the highest intensity in all samples, which indicates that the deposited Si wafers are located at this plane. Additionally, the peak related to the Si substrate appears at $2\theta = 28.4^0$. The observed diffraction peaks for all the samples are well-matched with the standard spectra in the ICSD (card no. 01-080-0074; a = 3.2535 nm and c = 5.2151 nm). Furthermore, the XRD spectra of samples A and C show that the ZnO nanorods grown on ZnO (85 nm)/Ti (10 nm)/Si and Zn (55 nm)/Ti (10 nm)/Si are well aligned along the c-axis, with no extra diffraction peak observed, suggesting that the Ti buffer layer has an amorphous phase, as reported by Kwak et al [20]. Obviously, all the samples have typically narrow FWHM in the range of 0.1°–1° [21]. Table 2 presents a synopsis of the data obtained from the XRD analysis of ZnO nanorods grown on p-type Si (111) with (A) {Ti (10nm)/ZnO (85nm)}, (B) {ZnO (85nm)}, (C) {Ti (10nm)/Zn (55nm)} and (D) {Zn (55nm)}. The strain ε_z (%) of the ZnO nanorods along the c-axis can be determined using the underlying equation [17]:

$$\varepsilon_z = \frac{Z - Z_o}{Z_o} \times 100\ \% \qquad (1)$$

where Z denotes the lattice parameter of ZnO NRs calculated from XRD data and Z_o refers to the unstrained lattice parameter of ZnO. Higher reduction of lattice mismatch was achieved between ZnO NRs, ZnO seed layer and Si substrates for sample (A) compared to sample (B) or sample (C) compared to sample (D) because of the use of Ti (10 nm) as a buffer layer [11]. In addition, the lattice mismatch between ZnO NRs, ZnO (85 nm) seed layer and Si substrates is lower than the lattice mismatch between ZnO NRs, Zn (55 nm) seed layer and Si substrates. The results of XRD analysis are consistent with the FESEM and TEM results. In general, this study confirms the synthesis of high-quality ZnO nanorods using the sonochemical method.

Table 2 XRD analysis of ZnO nanorods grown on p-type Si (111) with (A) {Ti (10nm) / ZnO (85nm)}, (B) {ZnO (85nm)}, (C) {Ti (10nm)/ Zn (55nm)} and (D) {Zn (55nm)}.

sample code	**2θ (Deg.)**	**FWHM (Deg.)**	**c (Å)**	**ε_z (%)**
A	34.3935	0.2475	5.210891	-0.08
B	34.4059	0.2503	5.208983	-0.12
C	34.4068	0.2605	5.208953	-0.12
D	34.4130	0.2623	5.207897	-0.14

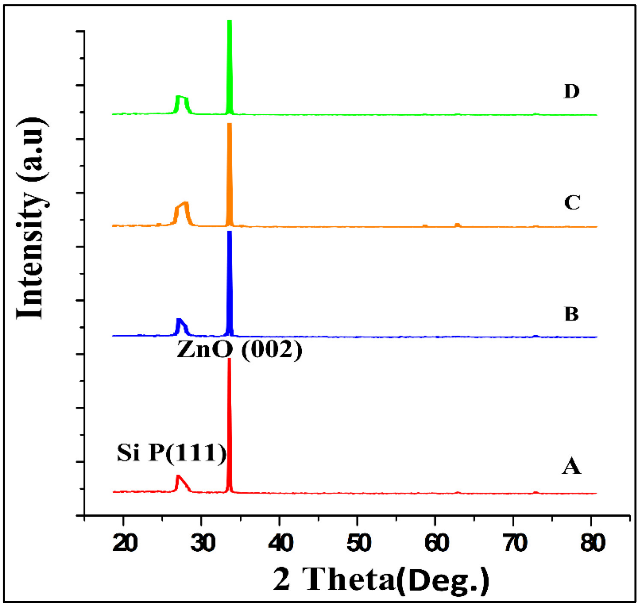


Fig. 4 XRD diffraction patterns of ZnO nanorods grown on p-type Si (111) with (A) {Ti (10nm) / ZnO (85nm)}, (B) {ZnO (85nm)}, (C) {Ti (10nm)/ Zn (55nm)} and (D) {Zn (55nm)}.

Conclusion

In this study, high-quality ZnO nanorods were successfully synthesized using the sonochemical method. Four different sets of ZnO nanorods were synthesized under the same conditions (concentration of Zn (NO3)2.6H2O & (CH2)6N4 = 0.05 M, amplitude = 40 % and time = 2 hours), but with different types and thickness of seed layers. The ZnO nanorods were synthesized on p-type Si (111) substrates using ZnO (85 nm) and Zn (55 nm) as seed layers with Ti (10 nm) as a buffer layer. The FESEM, EDX, EFTEM, and XRD clearly show that vertically aligned high-quality ZnO nanorods grown on {ZnO (85 nm) / Ti (10 nm)/ Si}, {ZnO (85 nm)/Si}, {Zn (55 nm) / Ti (10 nm)/Si}, and {Zn (55 nm)/Si}. However, the vertically aligned high-quality ZnO nanorods which were grown using ZnO (85 nm) have greater aspect ratio than those grown using ZnO (55 nm). Similarly, ZnO nanorods grown using ZnO as seed layer have lower compressive strains than those grown using Zn as a seed layer. This confirms that the thickness and type of a seed layer are key parameters to synthesize high quality ZnO nanorods using the sonochemical method. Finally, the lattice mismatch between ZnO NRs, seed layers and Si substrates was reduced due to introduction of Ti (10 nm) as a buffer layer.

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