Preparation and structural characterizations of ZnO nano-columns grown on porous silicon/silicon (PS/ Si (111)) by thermal evaporation

S. M. THAHAB

Materials Engineering Department, College of Engineering, University of Kufa, 00964-21 Najaf, Iraq

We have achieved growth of ZnO nano-columns (NCs) on porous silicon (PS)/Si(111) substrates, using commercial Zn powder by thermal evaporation in an atmosphere. Samples are annealed in wet oxygen and ambient argon gases of argon (Ar) gas. Structural and optical characterizations were performed using scanning electron microscopy (SEM), high resolution X-ray diffraction (HR-XRD) and photoluminescence (PL) spectroscopy. The obtained results of ZnO NCs indicated that the ZnO NCs on PS/ Si (111) substrates were of quite well-ordered and of good quality because the lattice mismatch between the ZnO NCs and substrates is small as compared to growth on some other substrates.

1. Introduction

ZnO nanostructures have been extensively studied because of their unique properties and promising applications in nanodevices and nanosystems [1–3]. The properties of ZnO nanostructures depend sensitively on both size and shape. Manipulation of their sub-structure and morphology has arisen many interests in recent years [4]. So far, a variety of Zn nanostructures such as nanowires, nanorods, nanodots, nanotubes, nanosheets, nanobelts, nanoribbons, nanorings, nanoaeroplanes, nanocombs, nanobridges and nanonails have been synthesized via various physical and chemical fabrication techniques [5–7]. These methods include vapor phase transport process, chemical vapor deposition, thermal evaporation process, electro deposition, hydrothermal, self-assembly, and template-assisted sol–gel process [8–10]. The porous silicon (PS) was first been discovered by Uhlir [11] in 1956. It has characteristics of high resistance, large internal surface and strong absorbability [12]. With the demonstration of room temperature photoluminescence from this material by Canham [13], although deposition of ZnO films on porous silicon substrates have been carried out, there were few reports concerning the effect of the pores in the porous silicon substrates on the crystalline properties of ZnO thin films to the best of our knowledge. In the present work, ZnO nanorods are deposited on porous silicon substrates by. The experimental findings on the effect of the sponge-like structure of the porous silicon substrates on the crystallinity properties of the ZnO nanorods are presented and the causes are discussed.

2. Experiment

In this work, the substrates Si wafer is ultrasonically cleaned with acetone and isopropyl alcohol (IPA), and then rinsed with distilled then cut to 2×2 cm^2 pieces and placed on a metal disk and sealed through an O-ring, so that only the front side of the sample is exposed to the electrolyte. When an Si wafer with high resistivity (i.e. more than a few mΩ/cm) is used, a high dose implantation on the back surface of the wafer is required to improve the electrical contact between the wafer and the metal disk. This step is crucial to get later homogeneity in the PS layer. This cell which is shown in Fig. 1 is the most widely used because it leads to uniform PS layers, allows an easy control of both porosity and thickness, and it is suitable for front side illumination of the sample during the attach. The synthesis is process was carried out in a controllable tube furnace with aquartz tube (inner diameter, 25 mm). A pure metallic Zn powder (99.9%) as source material was placed into a ceramic boat. The PS substrates (with the porous silicon (PS) side facing the source material) were inserted into a quartz tube within the furnace at a temperature of 400 ^{0}C.

To gather with the ceramic boat, the tube was positioned at the center of the tube furnace. Temperature was increased to 550, 600, and 650 ^{0}C under a continuous flow of highly pure argon (Ar) and wet oxygen(O_2) gases with flow rates of 350 sccm (Ar to O_2 ratio was(1:1) for 1h to examine the effect of heating temperature on the growth of ZnO nanostructure. After evaporation, the quartz tube was removed from the furnace and cooled to room temperature. A white layer of ZnO was observed on the PS substrate surface. The surface morphology and structure of the ZnO nanostructures were examined by scanning electron microscopy (SEM). The high- resolution PANalytical X-ray diffractometer (HR-XRD) was used for phase identifications. The photoluminescence (PL) spectra were obtained at room temperature using the Jobin Yvon Horiba HR800UV system with a 325 nm line of the He–Cd laser at power of 20 mW.
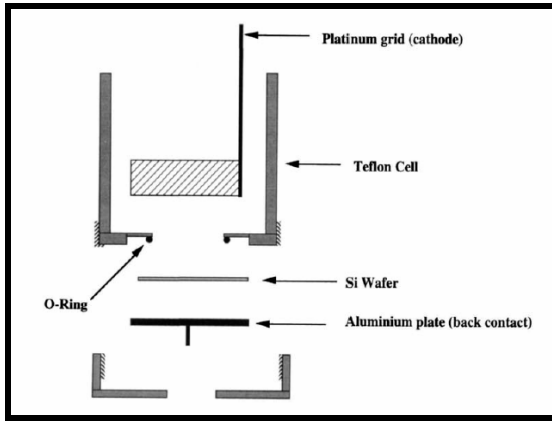
Fig. 1. Cross-sectional view of a 'conventional single-tank cell.

3. Results and discussion

The SEM image of the porous silicon (PS) substrate is shown in Fig. 2(a). It can be seen that the surface of the PS has a sponge-like structure, which consists of numerous inter connected nano-pore sand nano-silicon crystals with the homogeneous size of about 50 nm. The distribution of the pores is irregular. It also can be regarded as a nanocrystalline skeleton (quantum sponge) immersed in a network of pores [12]. Due to its special structure, PS is characterized by a very large internal surface area (of the order of 500–1000 m^2/cm^3) [12]. Such a large internal surface induces a large adsorption, which is another property of the porous silicon [12]. SEM images of the as synthesized ZnO NCs are shown in Fig. 1(b). Top view SEM images show an overview of high-density and ordered ZnO NCs on the PS (111) substrate side and ZnO deposited layer on Si side. The diameters of ZnO NCs range from 50 to 90 nm. The AFM result of the PS surface is shown in Fig. 3(a) for comparison with the surface morphology of the ZnO NCs /PS film measured by AFM which is shown in Fig. 3 (b). The From the AFM surface morphology measurement of the PS and ZnO NCs /PS surface, the RMS roughness is found increasing from 2.55 nm for the PS to 6.08 nm for the ZnO NCs. The increase in the RMS roughness is attributed to the partial filling and formations of ZnO NCs in the pores of PS. The surface of the porous silicon layer is composed of numerous nano-silicon crystals. The Si crystallites distributed randomly over the entire surface would act as nucleation sites, which induced ZnO NCs to grow along the preferred orientation.
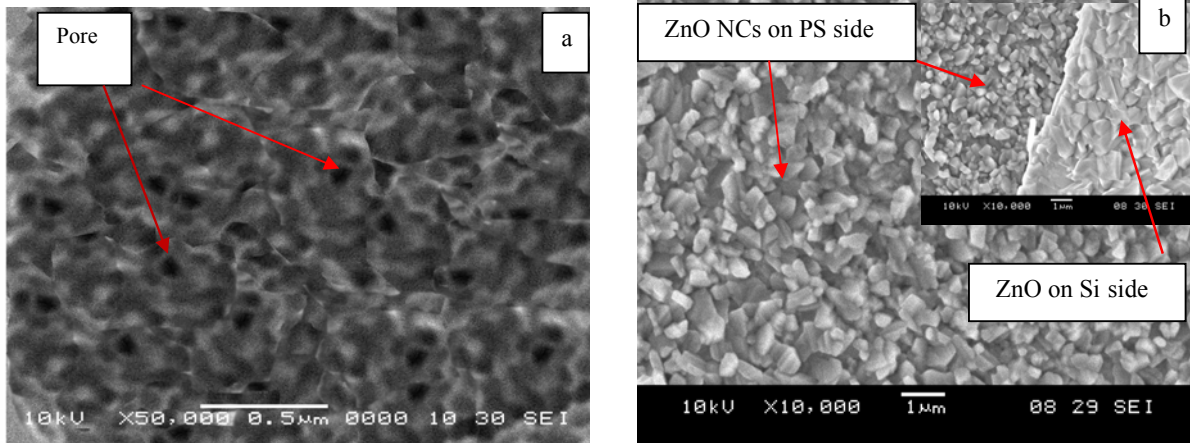

Fig. 2. SEM images of (a) PS and (b) ZnO NCs on PS substrate.
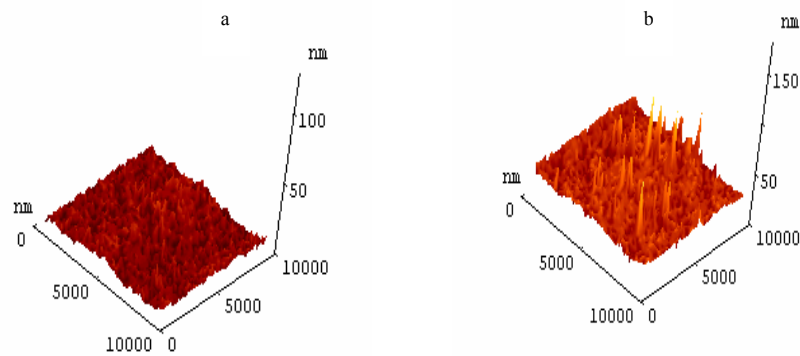

Fig. 3. AFM images of (a) PS and (b) ZnO NCs on PS substrate.

From the XRD and AFM results, it can be seen that the PS substrate can serve as a good template during ZnO NCs growth. Here it is proved that highly oriented crystalline ZnO NCs on PS substrate can be obtained by thermal evaporation. That is, the nucleation of the ZnO NCs initiated on protruding crystals on the rough porous substrate.The growth orientation and crystal alignment of ZnO NCs were investigated using HD-XRD techniques. All of the ZnO NCs exhibited a preferred c-axis orientation as shown in Fig. 4. It shows only the Bragg reflections that correspond to the ZnO (0002) and (0004) plane along with the substrate reflection, clearly indicating that the ZnO NCs had a single ZnO phase as well as a complete vertical alignment. This c-axis preferential growth is well known as a general habit of ZnO crystals since a (0001) basal plane of ZnO has the lowest surface energy. This indicates that the ZnO NCs are all highly c-axis oriented with the c-axis of the crystallite perpendicular to the substrate.

The reason of c-axis-oriented growth can be explained in terms of the low surface free energies of the (002) plane [14]. The (002) face is the high-density face and is the face with the lowest free energy. It can also see that for the ZnO NCs on the porous silicon substrate the intensity of the(002)-oriented peak (c-axis orientation)turns to be sharper, and the full-width half-maximum value to 0.30 on PS substrate is obtained. That is, the crystalline quality of ZnO NCs on PS substrate was significantly improved. These results implied that the PS substrate had some impact on improving the crystalline quality of the growth of ZnO NCs. The crystallitesizes of the prepared ZnO nanowires were calculated using the full width at maximum height (FWHM) of the (002) peak using Scherrer's formula (Eq.1).
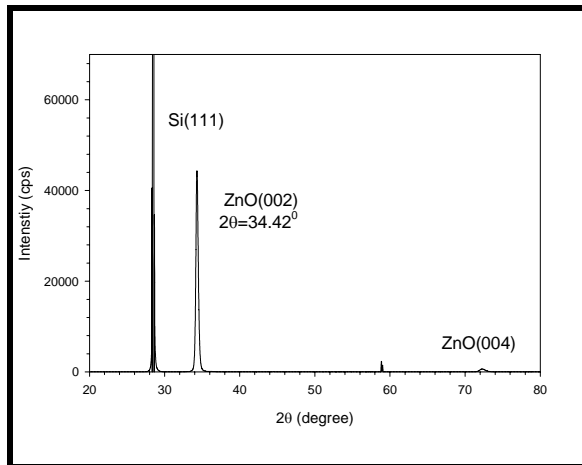

Fig. 4. HR-XRD of ZnO NCs on PS substrate.

$$D = \frac{0.9\lambda}{B \cos \theta} \qquad (1)$$

where λ is the X-ray wavelength, θ the Bragg angle of (002) peak, and B is the FWHM value. The grain size values were found around respectively.

The results show insignificant effect of the growth temperature on the crystallite sizes, and the average value of the size is 30 nm. PL spectrum of ZnO NCs product presented in Fig. 5 is detected with He-Cd laser used as the excitation source (with a wavelength of 325 nm) at room temperature.

Only a strong peak at around 3.31 eV, which is attributed to the near band edge emission, with no noticeable peak related to the defect level emissions around 2.2–2.5 eV, suggesting that they were of very high optical and crystalline quality. Only a broad peak located at 374.5 nm can be activated because the as-prepared ZnO NCs are too large for quantum confinement effects, ZnO NCs show very good emission property, which will be a great advantage in their photoemission application.

Table 1. Summarizes the ZnO NCs (002) diffraction peaks and FWHM at 2θ and grain size of the samples.

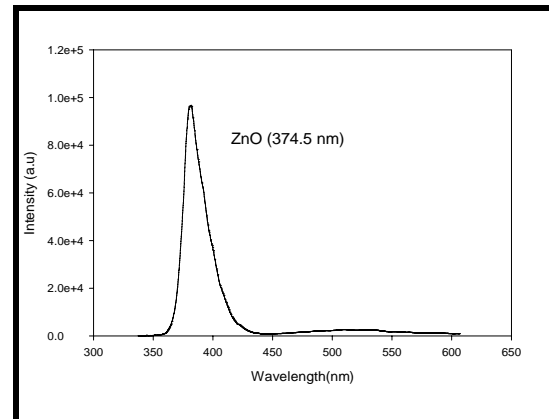| substrate	ZnO NCs (002) diffraction peak at 2θ	FWHM	grain size (nm)
PS (111)	34.42	0.30	30

Fig. 5. Photoluminance (PL) spectrum of ZnO NCs on PS substrate.

5. Conclusion

The structural, optical properties of ZnO NCs prepared by thermal evaporation on PS, substrate has been studied and investigated. The crystallinity, microstructure and surface morphology of ZnO NCs were investigated by X-ray diffraction (XRD) patterns scanning electron microscopy (SEM), atomic force microscopy (AFM) and photoluminescence (PL). The XRD spectra of all ZnO

NCs show mainly the ZnO (0 0 2) diffraction peaks of hexagonal wurtzite type structure. This indicates that ZnO NCs grew along c-axis orientation, perpendicular to the substrate. Only a broad peak located at 374.5 nm can be activated because the as-prepared ZnO NCs are too large for quantum confinement effects. These results implied that the PS substrate had some impact on improving the crystalline quality of the growth of ZnO NCs.

Acknowledgment

Refernces

[1] L. K. J. S., D. B. Janes, M. H. Yoon, A. Facchetti, T. Marks, J Nano Lett. **5**, 2281 (2005).
[2] Q. Ahsanulhaq, J. H. Kim, Y. B. Hahn, Nanotechnology **18**, 485307 (2007).
[3] K. Yubuta, T. Sato, A. Nomura, K. Haga, T. Shishido, J. Alloys Compd. **436**, 396 (2007).
[4] L. B. Feng, A. H. Liu, M. Liu, Y. Y. Ma, J. Wei, B. Y. Man, J. Alloys Compd. **492**, 427 (2010).
[5] Z. L. Wang, J. Phys.: Condens. Matter **16**, 829 (2004).
[6] T. Shishido, K. Yubuta, T. Sato, A. Nomura, J. Ye, K. Haga, J. Alloys Compd. **439**, 227 (2007).
[7] Z. Wang, X. F. Qian, J. Yin, Z. K. Zhu, Langmuir **20**, 3441 (2004).
[8] A. Umar, Y. B. Hahn, Nanotechnology **17**, 2174 (2006).
[9] H. Tang, J. C. Chang, Y. Y. Shan, D. D. D. Ma, T. Y. Lui, J. A. Zapien, C. S. Lee, S. T. Lee, J. Mater. Sci. **44**, 563 (2009).
[10] D. B. Wang, C. X. Song, Z. S. Hu, Cryst. Res. Technol. **43**, 55 (2008).
[11] A. Uhlir, BellSyst. Tech. J. **35**, 333 (1956).
[12] O. Bisia, O. S. Stefano, L. Pavesic, Surf. Sci. Rep. **38**, 126 (2000).
[13] L. T. Canham, Appl. Phys. Lett. **57**, 1046 (1990).
[14] N. H. Tran, A. J. Hartmann, R. N. Lamb, J. Phys. Chem. **B103**, 4264 (1999).

[*]Corresponding author: sabahmt@eng.kuiraq.com; sabahmr@yahoo.com