Advances in Engineering Research, volume 112
4th International Conference on Renewable Energy and Environmental Technology (ICREET 2016)

Effects of PLD deposited ZnO seed layer on the structure and morphology of ZnO nanowires prepared by CBD method

Shan-shan Lu[1, a], Ying Huang[1, b], Jia-yuan Qin[1], Zu-kang Mo[1], Wu-lin Xie[1], Yue-chun Fu[1], Huan He[1], Li-feng Bian[2], Shu-long Lu[2], Xiao-ming Shen[1, c]

[1] Guangxi Key Laboratory of Processing for Nonferrous Metal and Featured Materials, College of Materials Science and Engineering, Guangxi University, Nanning, 530004, China

[2] Key Laboratory of Nanodevices and Applications, Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Suzhou, 215123, China

[a]1393901254@qq.com, [b]hyamps@163.com, [c]docsjh@gxu.edu.cn

Keywords: ZnO seed layers, crystallinity, pulsed laser deposition, chemical bath deposition.
Abstract. ZnO seed layers have been deposited on ITO substrates by pulsed laser deposition (PLD) at different substrate temperatures. The crystalline structure, morphology of ZnO nanowires were characterized by X-ray diffraction (XRD), atomic force microscopy (AFM) and scanning electron microscopy (SEM). The effects of different seed layers on the crystalline structure and morphology of ZnO nanowires were investigated. The results show that the hexagonal wurtzite structure of ZnO seed layers are obtained when the substrate temperature is 200˚C. However, the ZnO seed layers are amorphous films at 150˚C. Vertically aligned ZnO nanowires are obtained by suitable CBD method on the ZnO seed layers with good crystallinity.

Introduction

In recent years, dye sensitized solar cells (DSSCs) have received great attention as one of the third generation solar cells, because of their cheap raw materials, simple production process, high photoelectric conversion efficiency and environmental friendliness [1]. As a wide band gap semiconductor, TiO_2 has played a significant role in the dye sensitized solar cells [2]. However, with the rapid development of DSSCs, researchers are now looking for other semiconductor materials which can replace TiO_2, such as CdSe, CdS and ZnO [3]. Among these candidates, ZnO is the most potential light absorbing material, due to its wide band gap (~3.37eV), high electron mobility, and its good optical, electrical, magnetic and piezoelectric properties. Therefore, it can be used to make light emitting diodes, thermoelectric devices and gas sensors, and so on [4]. Besides, as an electrode material, ZnO can improve the absorption of sensitization agent, electron transport rate and light absorption by light trapping effect [5]. At present, there are many different methods to prepare ZnO, for instance, chemical vapor deposition (CVD) and spray pyrolysis, etc. But they are expensive and complex which are not suitable for industrial production [6]. On the other hand, chemical bath deposition (CBD) is a better choice due to its lower cost and simpler requirement for equipment.

In this paper, ZnO seed layers were prepared on ITO substrates by pulsed laser deposition (PLD). Then ZnO nanowires were grown on ZnO seed layers by chemical bath deposition (CBD) method. The effects of different ZnO seed layers and processing parameters on the morphologies of ZnO nanowires have been investigated in detail, which help us obtain optimal conditions for preparing high length-diameter ratio ZnO nanowires for their applications in dye sensitized solar cells.

Experimental

ZnO seed layers were prepared by LMBE-450 pulsed laser deposition system. First, the ITO substrates were cleaned by ultrasonic cleaner in acetone, ethyl alcohol and de-ionized water for 10 min, respectively. Second, ZnO seed layers were deposited on ITO substrates for 1 hour by ablating the ZnO ceramic target (99.99%) using KrF pulsed laser (248nm). The substrate temperature was varied from 150˚C to 200˚C. Finally, the seed layer was annealed under vacuum condition at 200˚C for 1 h after deposition.

The ZnO seed layered ITO substrates were immersed in the aqueous solutions consisting of 50mM of hexamethylenetetramine, 50mM of zinc nitrate hexahydrate, 4.5M of polyethyleneimine (PEI). Hydrothermal syntheses were carried out at 95˚C for 9 h in the water bath. After the hydrothermal reaction, the ZnO nanowires grown on ITO substrates were rinsed with de-ionized water and then air dried. In the end, the ZnO nanowires were annealed in air at 400˚C for 30 min.

The crystalline structure of ZnO nanowire was characterized by X-ray diffraction (Rigaku D\MAX 2500). For the morphology evolution of the ZnO nanowires, atomic force microscope (Agilent 5500 AFM) and scanning microscope (Hitachi SU8020 FE-SEM) were used.

Results and discussions

The ZnO seed layers were grown on ITO substrate while the substrate temperature was set at150˚C and 200˚C. Fig.1 shows XRD patterns of ZnO seed layers deposited at various substrate temperatures. When the substrate temperature is 150˚C, the diffraction peaks in the XRD patterns correspond to the ITO substrate with no peaks from ZnO seed layer. It can be seen that the ZnO seed layers form amorphous films which have not crystal orientation. When the substrate temperature rises up to 200˚C, two diffraction peaks appear at 34.6°and 63.1°, corresponding to the (002) and (103) surfaces of hexagonal wurtzite structure ZnO. Obviously, the (002) peak is stronger than (103) peak, indicating that the ZnO seed layers are oriented along the c-axis direction.

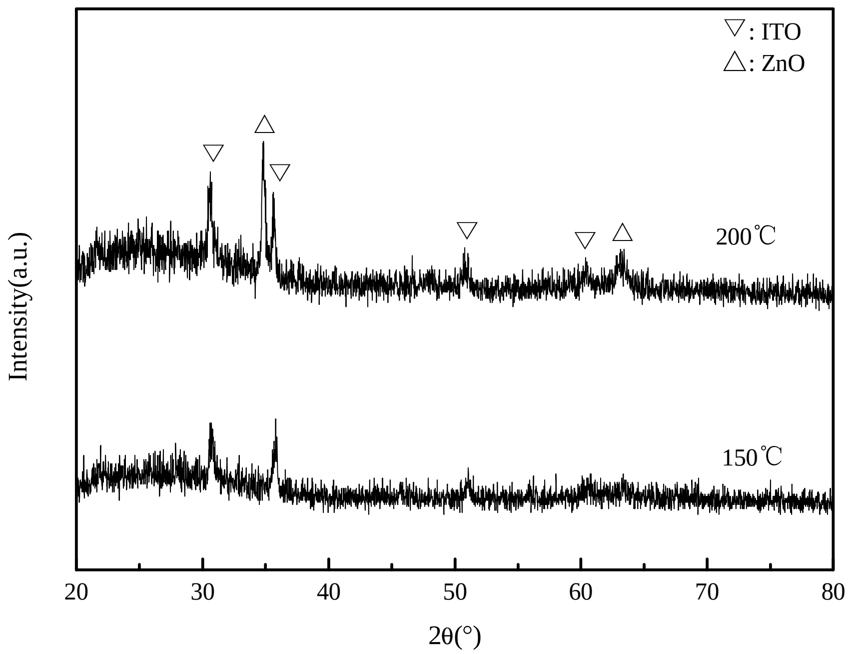

Fig.1 XRD patterns of ZnO seed layers deposited at different substrate temperatures

From the AFM images (as shown in Fig. 2), the ZnO seed layers are grown on the ITO substrate at different temperatures. For the effects of surface roughness of ZnO seed layers, Fig.2(a) shows that the surface of seed layer is relatively flat when the substrate temperature is 150˚C, but the crystallites with non-uniform size distribute randomly between the relatively flat areas. However, well-crystallized ZnO seed layers with uniform grain size are obtained when the substrate temperature set at 200˚C. All of the orientations of the grains are significantly perpendicular to the surface of the substrate, and have highly c-axis preferred orientation. When the substrate temperature is low, the slower migration of arriving adatoms on the substrate is not good for the growth of ZnO nucleation and helps the formation of amorphous structure. With the increase of the substrate temperature, the migration ability of deposited particles is so strong that grains have enough energy to move to the proper positions. Therefore, the crystal quality of ZnO seed layers is improved at relatively high temperature.

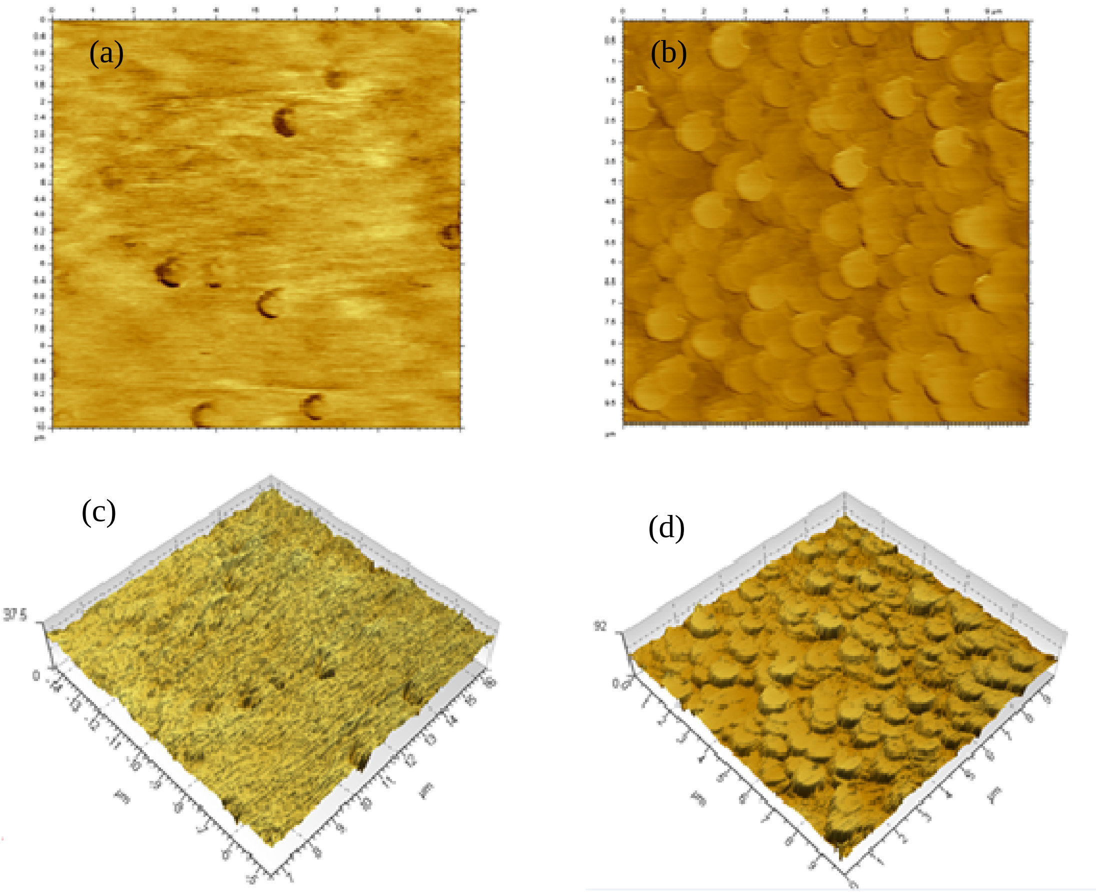

Fig.2 AFM patterns of ZnO seed layers evolve with substrate temperature (10μm×10μm) (a) and (c): 150˚C, (b) and (d): 200˚C

Fig.3 shows the SEM images of ZnO nanowires grown on different ZnO seed layers. It can be seen that the morphology of ZnO nanowires is obviously different, due to the various crystallinity and morphology of ZnO seed layers. In Fig.3(a) and (b), a substrate temperature of 150˚C results the shape of the cauliflower of ZnO nanowires with no definite orientation. The reason for this is that ZnO nanowires grow along the different directions of the seed layer grains, which are amorphous films with unordered arrangement. While the substrate temperature was raised up to 200˚C, not only the ZnO seed layers have good crystallinity but the ZnO nanowires almost arranged vertically at the substrate, as shown in Fig.3(c) and (d). In addition, the ZnO nanowires grow along the [0001] crystal direction of the seed layers, which are confirmed by the results of XRD measurement.

The ZnO is a typical polar crystal, because Zn atoms in the c-axis are asymmetrically distributed and in favor of the c-axis. Besides, in the c-axis direction, the crystallographic orientation of the $[ZnO4]^{4-}$coordination tetrahedron is different, and its deviation is 60° between upper and lower layers. Therefore, the (0001) plane of Zn atoms are positive surface while the (000-1) plane of Oxygen atoms are negative surface [7]. The positive surface is covered by positive charges that (0001) surface attracts negative charges, such as OH^-, and then alternately attract ZnO^{2+} and OH^-. Therefore, nucleation and growth of the ZnO occur on the (0001) surface. The growth rate of ZnO on (0001) surface is faster than that on the lateral surface, resulting in the ZnO nanowires grown along c-axis.

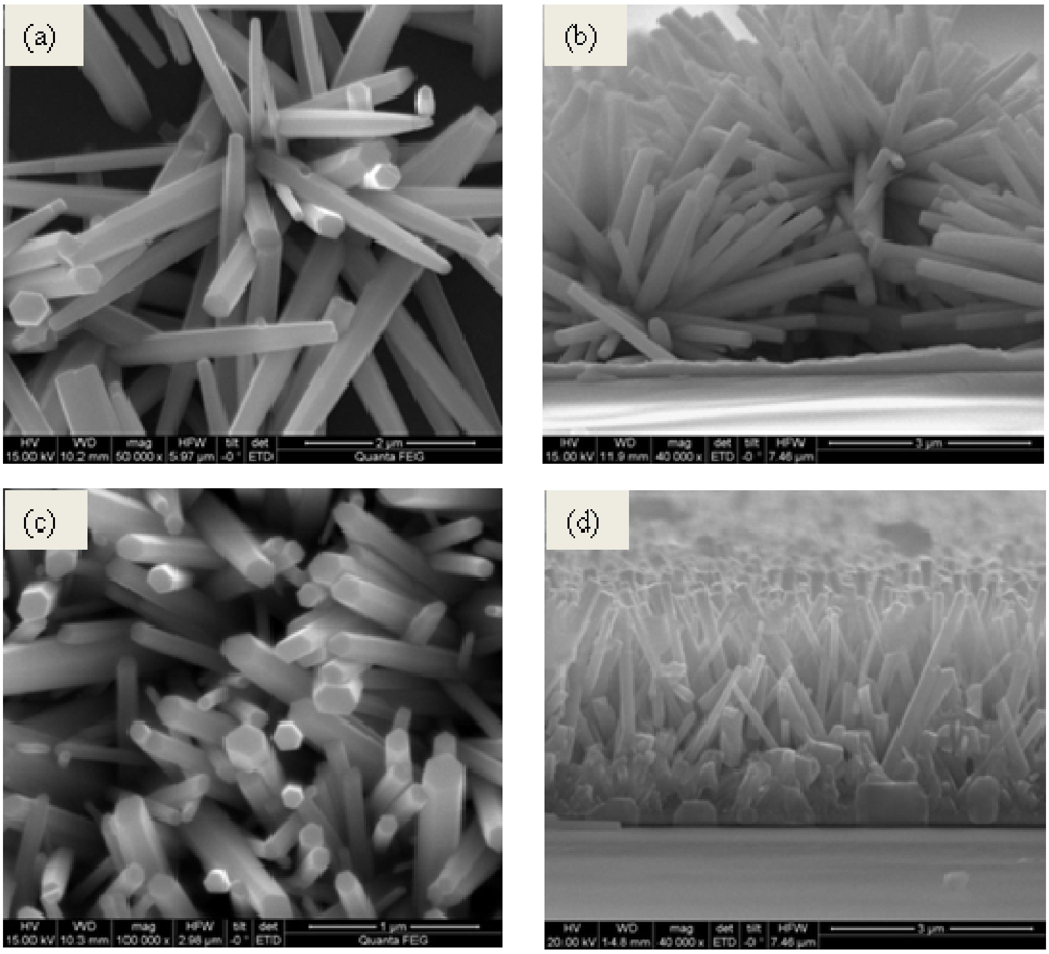

Fig.3 SEM images of the ZnO nanowires grown on different ZnO seed layers (a) and (b)150˚C, (c) and (d) 200˚C

In a word, with the preferential growth along the (0001) surface, ZnO seed layers can vertically aligne on the ITO substrate when the substrate temperature was 200˚C. However, when the substrate temperature was 150˚C, the ZnO seed layers formed amorphous films, and the ZnO nanowires grow along various directions from the disordered crystallites. Gradually, the ZnO nanowires formed the shape of the cauliflowers. Fig 4 shows the schematic diagram of ZnO nanowires grown on different ZnO seed layers deposited at different substrate temperatures.

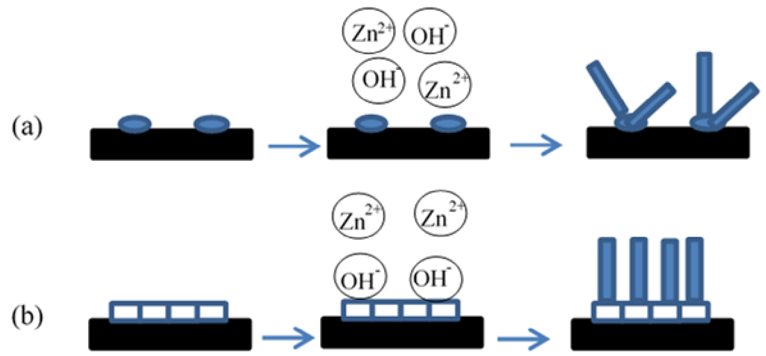

Fig.4 Schematic diagram of ZnO nanowires grown on different ZnO seed layers deposited at different substrate temperatures of (a) 150˚C and (b) 200˚C

Conclusions

In this study, the ZnO seed layers have been successfully prepared by the pulsed laser deposition system. When the ZnO seed layers were deposited on ITO substrate at 200˚C, the ordered arrangement with hexagonal wurtzite structure was obtained, and the disordered amorphous ZnO seed layers were prepared at 150˚C. Vertically aligned ZnO nanowires are obtained based on the good crystallinity of ZnO seed layers, indicating the effects of different seed layers on the crystalline structure and the morphology of ZnO nanowires.

Acknowledgements

This work was financially supported by the National Natural Science Foundation (61474030), the Guangxi Natural Science Foundation (2015GXNSFAA139265), the Open Foundation of Key Laboratory of Nanodevices and Applications, Chinese Academy of Sciences (15ZS06), the Foundation of Guangxi Science & Technology Development Project (1598008-15) and the Foundation of Nanning Municipal Science & Technology Development Project (20151268).

References

[1] M. Law, L. Greene, J.C. Johnson, R. Saykally, P.D. Yang: Nature materials Vol. 4 (2005), p. 455

[2] J.F Lei, S.L. Liu, K. Du, S.J. Lv, C.J. Liu, L.Z. Zhao: Electrochimical Acta Vol. 171 (2015), p. 66

[3] Y.M. Meng, Y. Lin, J.Y. Yang: Journal of solid state chemistry, Vol. 210 (2014), p. 160

[4] J. Zhang, X. Li, W. Guo, et al.: Electrochimica Acta Vol. 56(9) (2011), p. 3147

[5] Q.W. Jiang, G.R. Li, S. Liu, et al.: Journal of Physical Chemistry C Vol. 114(31) (2010), p. 13397

[6] V. Bhavanasi, C.B. Singh, D. Datta, V. Singh, et al.: Optical Materials Vol. 35 (2013), p. 1352

[7] Z.X. Ma, Y.Z. Jiang, et al.: *Principle and technology of nanometer ZnO* (Light Industry Press, Beijing: China 2007).