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ScienceDirect

Procedia Materials Science 8 (2015) 630 – 634

Procedia Materials Science

www.elsevier.com/locate/procedia

International Congress of Science and Technology of Metallurgy and Materials, SAM - CONAMET 2013

Study of the Substrate Influence in ZnO Nanowires Oriented Growth

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Abstract

A solution growth approach for zinc oxide (ZnO) nanowires is highly appealing because of the low growth temperature and possibility for large area synthesis. In our work, ZnO nanowires were obtained from thin films prepared on silica glass, Si (100) and Si (111) from a single and five layers spin-coating deposition of a sol–gel prepared with dehydrate zinc acetate, monoethanolamine and isopropanol. Crystallization annealing was performed at 450 °C. These films were used as seed layer to prepare ZnO nanowires/nanorods from a zinc nitrate and hexamethylenetetramine solution. X-ray diffraction analysis showed that nanowires/nanorods grown on Si (111) were preferentially orientated along the [002] direction.

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*Keywords:*Silicon, Silica Glass, Nanowires, ZnO

1. Introduction

In recent years, semiconductor nanowires have been studied by many research groups because of their unique optoelectronic properties [Duan et al. (2003), Duan et al. (2001), Li et al. (2006)]. Among the semiconductor oxide nanowires, ZnO is one of the most promising materials due to their direct band gap of 3.3 eV and its high exciton binding energy (60 meV) at room temperature. This makes ZnO nanowires a valuable material for many different technological applications, such as UV nanolasers [Huang et al. (2001)], field effect transistors [Cha et al. (2006)],

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Selection and peer-review under responsibility of the scientific committee of SAM - CONAMET 2013
doi:10.1016/j.mspro.2015.04.118

solar cells [Law et al. (2005)], nanogenerators [Wang and Song (2007)] and other applications in optoelectronic devices [Özgür et al. (2005)].

Among the most commonly used ZnO nanowires synthesis methods are gas condensation using catalytic reactions [Wu and Liu (2002), Yang et al. (2002)] and hydrothermal methods [Greene et al. (2006)]. It is possible to synthesize high aspect ratio crystalline ZnO nanowires by using gas-phase methods; however, its high synthesis temperature and vacuum requirements limits the substrate size and, therefore, integration into devices. Hydrothermal method, on the other hand, allows growth of ZnO nanowires at low temperature and atmospheric pressure over larger areas and on any type of substrate, having been able to obtain perfectly aligned ZnO nanowires [Greene et al. (2005)]. A problem that may be associated with the hydrothermal method is the time required for nanowires synthesis, ranging from hours to days [Law et al. (2005)]. Due to its versatility and simplicity, this method has been used by many investigators.

In this work ZnO nanocrystals were used as seed layers, obtained by sol-gel process and deposited on various substrates by spin coating technique. From these, nanowires were grown by hydrothermal method.

2. Experimental Procedure

ZnO nanowires/nanorods were grown on a ZnO seed layer prepared by sol-gel. Substrates used were silica glass, silicon (100), silicon (111) and silicon (111) with a 3.0 μm SiO_2 layer, obtained by wet oxidation. It was prepared 30 ml of 0.3 M solution of zinc acetate dehydrate ($Zn(CH_3COO)_2.2H_2O$) as precursor, monoethanolamine ($NH_2CH_2CH_2OH$) as a stabilizer (1:1 ratio with zinc) and isopropanol as solvent [Li et al. (2005)]. This solution was dissolved by stirring in a 60ºC bath for one hour, resulting transparent. Before the seeding, substrates were cleaned with piranha solution in 3:1 ratio. After aging the solution during 24 h, 1 and 5 layers were deposited on substrates by spin coating method at 3000 RPM for 20s. Between layers, drying was performed at 60ºC during 15 min to consolidate the deposited material. Subsequently, final heat treatments were performed at 450ºC for 1 h for ZnO crystallization and to eliminate organic residues.

Using hydrothermal method based on Greene et al. [Green et al. (2005)] development, oriented nanowires were synthesized. Substrates with seed layers were submerged in a 0.1 M zinc nitrate hexahydrate solution in a relation 1:1 with hexamethylenetetramine (HMT) and heated in a 95ºC bath.

Growth of oxide nanowires/nanorods from a solution, require a pH control to avoid precipitation on substrate due to the hydrolysis and condensation reactions of metallic ions and their complexes. In the solution used in the hydrothermal method, the HMT decomposes in formaldehyde and ammonia, acting as a buffer solution providing hydroxides in a slowly way. Throughout the process, pH was kept between 6-7.

After 3 hours, samples were removed from the growing solution and rinsed with deionized water and dried in an oven at 200ºC for 10 min.

Table 1. ZnO nanowires samples.

	Samples	Substrate	Oxidation
1 seed layer	S100_s1	Silicon (100)	-
	S111_s1	Silicon (111)	-
	S111ox_s1	Silicon (111)	0.3 μm
	VS_s1	Silica Glass	-
5 seed layer	S100_s5	Silicon (100)	-
	S111_s5	Silicon (111)	-
	S111ox_s5	Silicon (111)	0.3 μm
	VS_s5	Silica Glass	-

Table 1 introduces the nomenclature and a description of synthesized samples, indicating substrate used and the thickness of the layer for oxidized ones.

Crystalline structure of ZnO nanowires/nanorods was analyzed with X-Ray diffraction (XRD), using a Philips PW 3710 conventional equipment, with Cu-K radiation (1.54056 Å). The morphology and size of ZnO nanowires/ nanorods were observed with a Field Emission Scanning Electron Microscope (FESEM) Karl Zeiss DSM 982 Gemini.

3. Results and discussion

Figures 1.a and 1.b show the ZnO nanowires diffraction patterns on silicon and silica glass substrates, respectively. Observed diffraction peaks correspond to ZnO wurzite structure [JCPDS Nº 36-145]. In samples grown on Si (111), (002) orientation is presented with greater intensity.

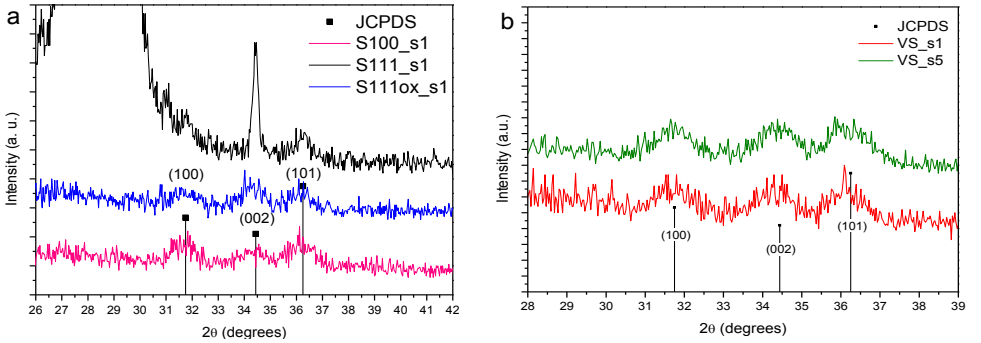

Fig. 1.Diffractograms from samples: (a) S100_ s1, S111_ s1 and S111ox_ s1; (b)VS_s1 and VS_s5.

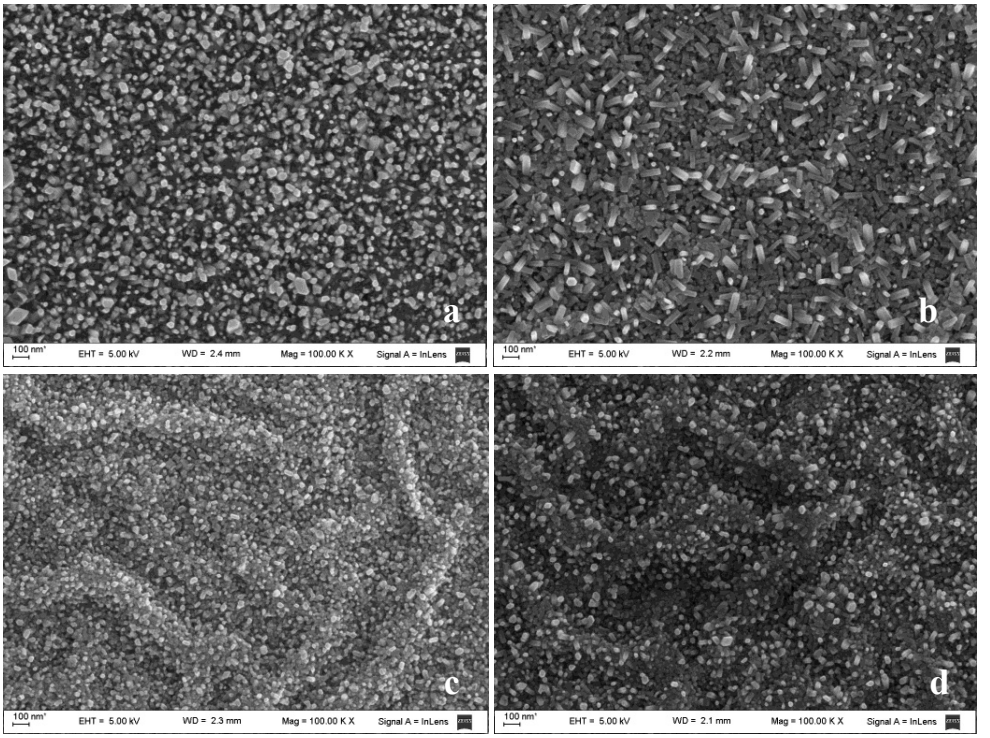

Fig. 2.FESEM micrographs of samples:S111_ s1 (a), S100_ s1 (b), S111_ s5 (c) and S100_ s5 (d).

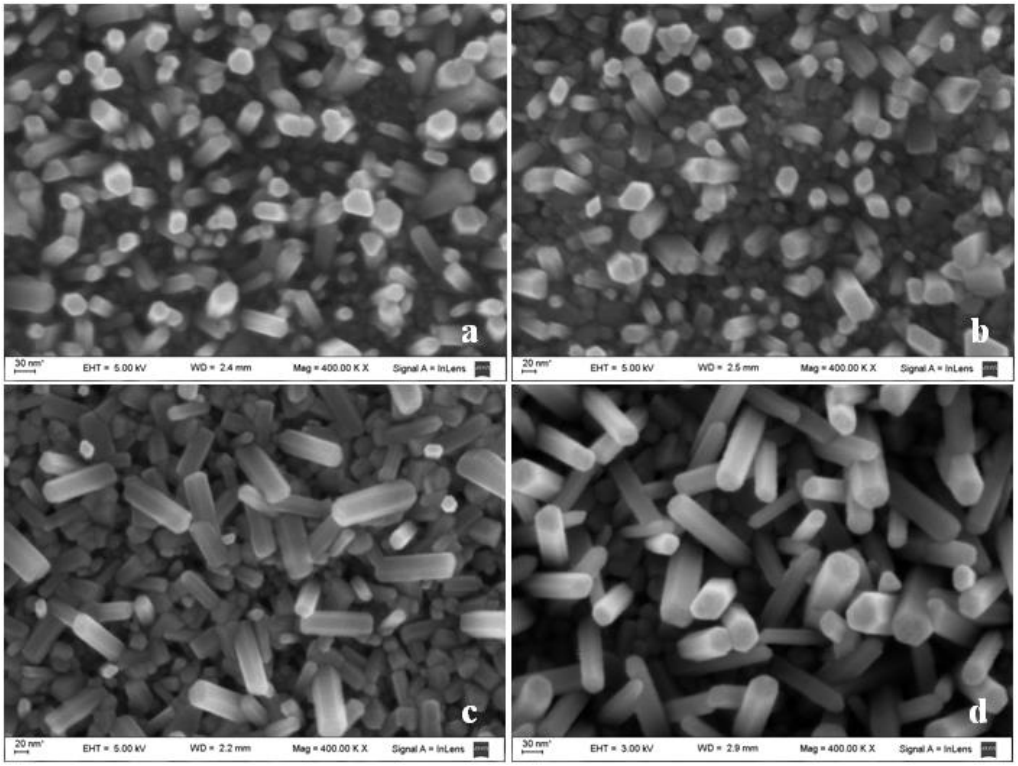

Fig. 3.FESEM micrographs of samples: S111_ s1 (a), S111ox_ s1 (b), S100_ s1 (c) and VS_s1 (d).

In Figure 2, it can be observed the FESEM micrographs of the ZnO nanowires/nanorods grown on silicon and silica glass substrate. The images with lower magnification show the growth density on the substrate; meanwhile the ones with higher magnification (Figure 3) allow seeing the hexagonal shape of ZnO nanowires, related with crystalline structure.

It would be expected that the nanowires preferential growth orientation is directly related with the ZnO seed layer [Kenanakis et al. (2009)]. In turn, heat treatment conditions influence, among other factors, the nanocrystal orientation of seed layer [Casanova et al. (2011)], defining nanowires characteristics. Therefore, it can be achieve ordered ZnO nanowires by controlling the crystal orientation of the ZnO seed layer. In this work, where the heat treatment conditions of seed layers were maintained constant, the nanowires orientation is fundamentally related with the substrate used. The nanowires/nanorods grown on silicon present a higher orientation upon [002] direction than those grown on silica glass. In turn, (002) orientation is more promoted in silicon (111) than in silicon (100). By increasing the number of coats, the ratio of main peak height becomes similar to the ZnO powder randomly oriented (Figure 3).

The nanowires diameter was measured from digital images with Image Tool [Wilcox et al. (2002)]. The following histograms (Figure 4) present the diameter distribution of nanowires/nanorods. All samples show an average nanowires diameter about 30 nm, regardless the used substrate. As well, the aspect ratio was measured, obtaining a height-diameter relation of 2.6, 2.1 and 2.9 in S100_s1, S111_s1 and S111ox_s1 samples, respectively. It can be observed that nanowires grown on oxide substrates present a higher relation aspect compare to those without oxidation treatment.

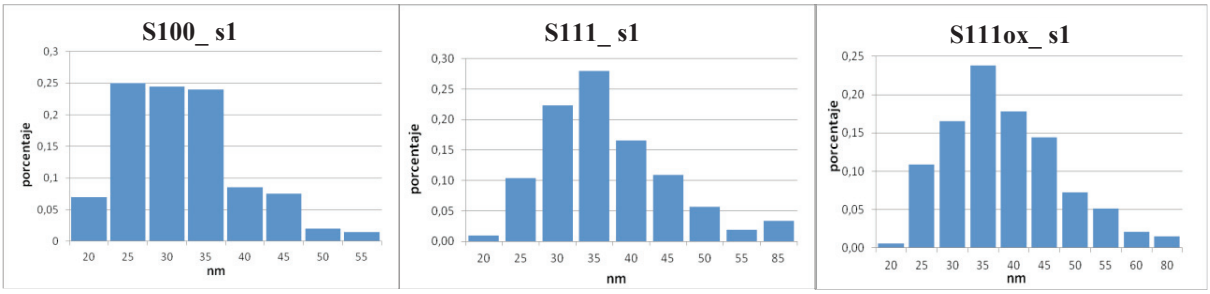

Fig. 4.Histograms from samples S100_ s1, S111_ s1 and S111ox_ s1.

4. Conclusion

It has been proved a simple and economical method for the synthesis of well aligned ZnO nanowires from a hydrothermal method. The nanowires show a better orientation on silicon substrate, in particular the (111) direction. Substrates where were deposited a single coat as seed layer also present better orientation.

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