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GROWTH OF ZnO 1-D NANOSTRUCTURES BY CHEMICAL BATH DEPOSITION METHOD USING TEXTURED ZnO SEEDS*

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ABSTRACT

A simple method has been developed to synthesize ZnO one-dimensional nanostructures on glass substrates from aqueous solution. The solution-based synthesis of oxide 1D nanostructures enables the fabrication of the next-generation of nano-devices at low temperature.

ZnO 1D nanostructures were grown on seeded glass substrates using zinc nitrate hexahydrate as the source of Zn, at temperatures up to 90℃. The morphology, crystalline structure and optical properties of the obtained nanostructures were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and optical spectra.

KEYWORDS: ZnO, chemical bath deposition, 1D nanostructures, seed layer, morphology, optical properties

1. Introduction

Zinc oxide (ZnO) is an interesting II–VI semiconductor because of its wide direct band gap of ~ 3.3 eV and large free-exciton binding energy of ~ 60 meV. On account of its various remarkable properties, such as excellent chemical and thermal stability, high-transparency in the visible region, near-UV emission, biocompatibility, and wide electrical conductivity range, ZnO is an excellent candidate for various electronic and optoelectronic devices [1, 2, 3].

Also, a lot of ZnO nanostructures have been reported, such as nanobelts (NBs), nanotubes (NTs), nanorods (NRs) or nanowires (NWs), and so forth [4]. One-dimensional semiconductor nanorod /nanowire structures have been widely used recently because of their special properties of quantum confinement, high surface-to-volume ratio, higher optical gain, faster response, and specific crystalline orientation [5].

ZnO nanorod/nanowire structures, in particular, have attracted a great attention in the last years due to their applications in sensors, cantilevers as well as in optoelectronic devices such as light-emitting diodes and excitonic solar cells [6].

Over the past few years, ZnO nanorods and nanowires have been synthesized with various methods including vapor-liquid-solid (VLS) epitaxy, chemical vapor deposition (CVD), pulse laser deposition (PLD), deposition within anodic alumina membrane channels, aqueous solution method, and so on. Aqueous solution approaches for the growth of ZnO nanostructures are considered advantageous, compared with other methods, mainly due to low growth temperature and good potential for large-scale production [7, 6].

In the present paper, we report the two steps synthesis of zinc oxide nanorod/nanowire arrays by a spin-coating method followed by a simple chemical bath deposition.

The effects of process parameters, seeded substrates and solution concentration, on the morphology, microstructure and optical properties of ZnO were investigated in details.

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2. Experimental procedure

All the reagents (analytical grade purity) were purchased from Sigma Aldrich. They were used as received without any further purification.

The growth of ZnO nanorods/nanowires was carried out from aqueous solution of zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$) and hexamethylenetetramine (HMT, $C_6H_{12}N_4$), by chemical bath deposition (CBD) method. Before coating, the glass substrates were cleaned with acetone in an ultrasonic bath and etched by piranha solution (2:1 mixture of concentrated H_2SO_4/30% H_2O_2). The as-grown ZnO nanowires were rinsed in deionized water and dried for 30 min at 90^{o}C for further characterization.

The *morphology* of obtained zinc oxide nanostructures were examined by scanning electron microscopy using a FEI Nova NanoSEM 630 - (SEM, Hitachi S-4200 and FE-SEM JEOL JSM-7000F). *The crystalline structure and orientation* of the 1D nanostructures were recorded at room temperature using a Rigaku SmartLab diffractometer, with Cu Kα radiation. *The optical transmission spectra* of the films were acquired at room temperature with a Perkin Elmer Lambda 35 spectrometer, operated in air, at normal incidence, in the 300 nm – 1100 nm spectral range. From the optical measurements, *the optical energy gap*, Eg, was calculated assuming a direct transition between the edges of the valence and the conduction bands, for which the variation in the absorption coefficient, α, with photon energy, hν, is given by the equation:

$$(\alpha h\nu)^2 = B(h\nu - Eg) \quad (1)$$

By plotting $(\alpha h\nu)^2$ versus hν and extrapolating the linear region of the resulting curves, Eg was obtained.

Raman spectra measurements were carried out on Raman spectrometer (LabRAM HR 800 Raman Spectrometer). The He-Ne laser with wavelenght 633 was used as a source of excitation.

3. Results and discussion

In the reaction for growing the zinc oxide nanoarrays, the HMT plays an important role. It decomposes to formaldehyde and ammonia, which acts as a *p*H buffer and supply of OH^- ion slowly [3, 4, 8-10].

The main chemical reaction process can be described as follows:

$$(CH_2)_6N_4 + 6H_2O \rightarrow 6HCHO + 4NH_3 \quad (2)$$
$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \quad (3)$$
$$2OH^- + Zn^{2+} \rightarrow Zn(OH)_2 \quad (4)$$
$$Zn(OH)_2 \rightarrow ZnO + H_2O \quad (5)$$

Figure 1 shows that higher solution concentration leads to larger diameter of zinc oxide nanowires. The average diameters of the as-prepared samples grown from solutions of 0.01 M, and 0.025 M are 14 nm (Fig. 1a) and 25 nm (Fig. 1b), respectively.

In addition, it can be observed an increase of the density of ZnO NWs on the substrate when the concentration of aqueous solution increases.

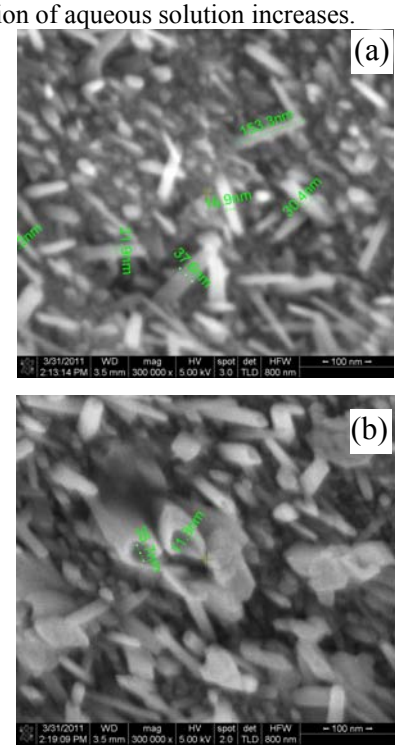
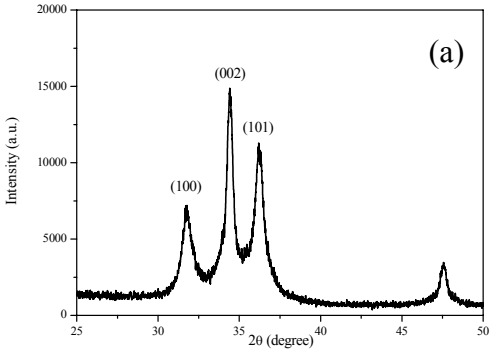


Fig 1. *SEM imagines of ZnO 1D nanomaterials grown aqueous solution of (a) 0.01M and (b) 0.025M.*

Figure 2 presents the XRD patterns of the grown ZnO nanowires.

These patterns show, in the 2θ range 25-50, the most important three peaks of hexagonal wurtzite type of ZnO structure. One can notice from the XRD data that all samples are polycrystalline and exhibit single phase ZnO hexagonal wurtzite structure with *c*-axis (002) oriented.



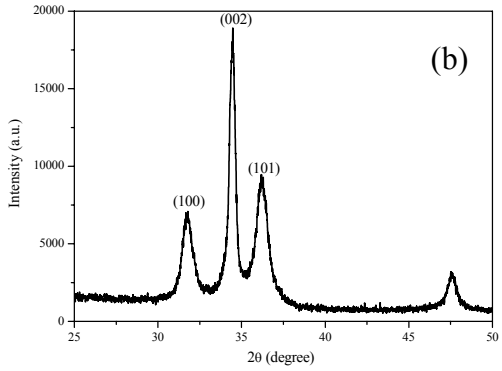


Fig.2. *XRD patterns of ZnO 1D nanomaterials grown from solution of (a) 0.01M and (b) 0.025M.*

The intensity of (002) diffraction peak is higher than the intensity of other peaks, which indicates the nanowires are highly *c*-axis oriented and normal to the substrate surface. The intensity of (002) plane increases when the molarity of aqueous solutions of $Zn(NO_3)_2$ and $C_6H_{12}N_4$ increases. Figure 3 shows the optical transmittance spectra of the films in the wavelength region range from 300 to 1100 nm. Transmittance in the visible and near-infrared regions exceeds 50% for all samples with a sharp ultraviolet absorption edge around 374 nm.

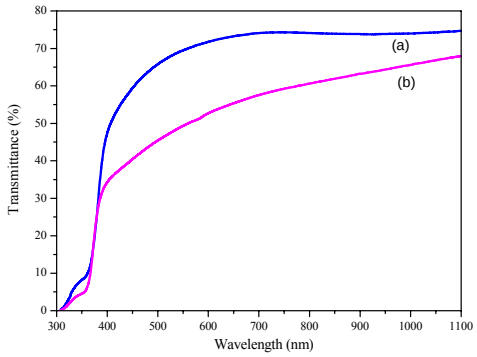


Fig. 3. *Optical transmittance spectra of samples obtained from solution of 0.01M (a) and 0.025M (b).*

In addition, the ZnO 1D nanostructures grown from the precursor concentrations of 0.025M presents a decrease in transmittance and shows a red-shift of absorption edge, which may be attributed to the increase of grain size.

The optical transmittance data have been used for the calculation of direct optical energy gap (Figure 4), according to the equation (1).

The band gap values decrease from 3.80 to 3.77 eV when the concentration solution increases from 0.01 to 0.025 M, respectively.

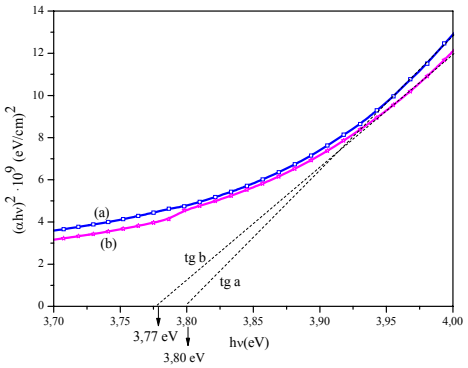


Fig. 4. *The plots of $(\alpha h\upsilon)^2$ vs. photon energy ($h\upsilon$) for samples obtained from solution of 0.01M (a) and 0.025M (b).*

The decrease of *Eg* can be attributed to the increase of grain size with increasing concentration. The band gap energy, a constant of bulk materials, varies in thin films due to particle size effect [10].

4. Conclusions

ZnO 1D nanostructures have been successfully synthesized on glass substrates by chemical bath deposition method.

The influence of the concentration of the precursor solution on the morphology, microstructure and optical properties of the obtained 1D nanostructres was studied.

The morphology is sensitive to the conditions of the preparation. X-ray diffraction data reveal that the as-grown 1D nanostructures has wirtzite structure with preferential orientation along the (002).

The optical transmittance decreases when the concentration increases. The optical band gap of the samples ranges from 3.79 to 3.77 eV when the precursor solution decreases.

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