SYNTHESIS AND CHARACTERIZATIONS OF ZINC OXIDE NANOSTRUCTURES

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Key words: Zinc oxide; ZnO; Nanostructures; Sol-gel; Large area electronics.

Abstract: Zinc oxide (ZnO) is an emerging optoelectronic material in large area electronic applications. We present the synthesis and the characterization of ZnO nanostructures. The ZnO nanostructures were synthesized using sol-gel hydrothermal technique on oxidized silicon substrates. The surface morphologies of the ZnO nanostructures were examined using scanning electron microscope (SEM) and atomic force microscope (AFM). The optical properties were measured using photoluminescence (PL) and ultraviolet-visible (UV-Vis) spectroscopies. The fabrication process and preliminary characterizations of the ZnO nanostructures will be described in this paper.

Sinteza in karakterizacija nanostruktur cinkovega oksida

Kjučne besede: cinkov oksid, nanostrukture, sol-gel, elektronika velikih površin

Izvleček: Cinkov oksid je nov optoelektronski material z možnostjo uporabe na področju elektronike velikih površin. V prispevku predstavljamo sintezo in karakterizacijo nanostruktur cinkovega oksida. Nanostrukture so bile sintetizirane z uporabo sol-gel hidrotermalne tehnike na oksidiranih silicijevih substratih. Površinske morfologije ZnO nanostruktur smo pregledovali s pomočjo vrstičnega elektronskega mikroskopa (SEM) in mikroskopa na atomsko silo (AFM). Optične lastnosti smo merili z uporabo fotoluminiscence (PL) in ultravijolične spektroskopije (UV-Vis). V članku so opisani tudi proces proizvodnje in preliminarne karakteristike nanostruktur cinkovega oksida.

1. Introduction

One-dimensional (1-D) zinc oxide (ZnO) nanostructures such as nanorods, nanoneedles, nanobelts and nanowires of desirable dimension have lately attracted significant attentions due to their unique electronic and optical properties compared to bulk structure /1-11/. The functional nanostructures posses excellent physical properties, owing to their geometry with high aspect ratio which modifies the light-matter interaction. The ZnO material has wide bandgap energy of 3.37 eV and large exciton binding energy of 60 meV, which make ZnO a promising candidate for many applications such as electronic, optoelectronic and information technology devices including sensors, displays, and solar cells /12/. However, in many applications both the size and the shape of the ZnO particles determine the material properties and therefore the performance of the devices /6,12/.

The 1-D nanostructured ZnO with different morphologies have been reported, for instances, nanorods, nanowires, nanobelts and quantum dots /1-11/. Several techniques have been employed to grow 1-D ZnO nanostructures, such as sol-gel technique, hydrothermal or solvothermal treatment, chemical precipitation method, molecular beam epitaxy and chemical vapor deposition. Among these techniques, the sol-gel method has distinctive advantages due to its lower crystallization temperature, ability to tune microstructure via sol-gel chemistry, conformal deposition ability, compositional control and large surface area coating capability /1/.

In this work, we realized the ZnO nanostructures using the sol-gel hydrothermal technique. The ZnO nanostructures were characterized using scanning electron microscope (SEM), atomic force microscope (AFM), photoluminescence (PL) and ultraviolet-visible (UV-Vis) spectroscopies. The ZnO nanostructures were formed on the oxidized silicon (100) substrates. The fabrication process and preliminary characterizations of the ZnO nanostructures will be described in this paper.

2. ZnO Fabrication Process

The fabrication process of the ZnO nanostructures is depicted in Figure 1. Silicon (Si) (100) substrate used for the growth of ZnO nanostructures was cleaned and etched in diluted hydrofluoric acid. The Si substrate was then rinsed and cleaned with de-ionized water. After that, the seed layer of silicon oxide (SiO_2) was grown on the Si substrate. The SiO_2 seed layer is necessary in order to enhance the growth of the ZnO nanostructures on the Si substrate, since there is a lattice mismatch between Si and zinc /13/. The oxidation process was carried out in 1 atmospheric ambi-

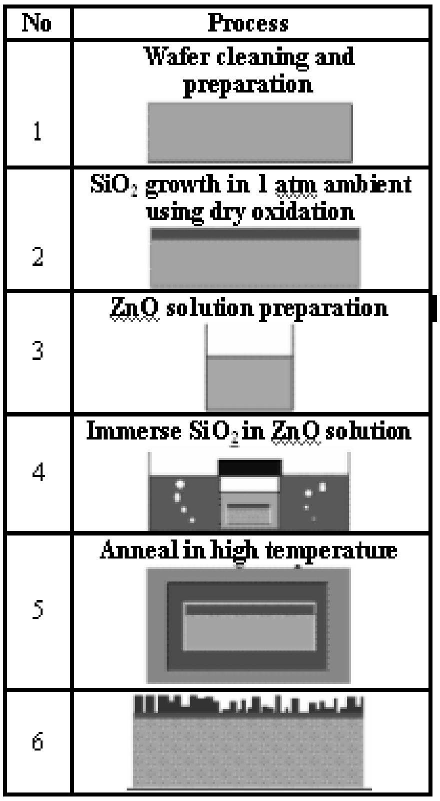

Fig. 1: Sol-gel hydrothermal fabrication process of the ZnO nanostructures.

ent and 900 °C for 20 minutes. Solution for ZnO nanostructures growth was prepared using an aqueous solution of zinc nitrate hexahydrate [$Zn(NO_3)_2.6H_2O$] mixed with hexamethylenetetramine [$C_6H_{12}N_4$] at molarity (M) of 0.01 M. The solution was diluted in 200 ml de-ionized water. The solution was then stirred at 60 °C for 2 hours and aged at room temperature for 24 hours. The oxidized Si substrate was immersed in the solution at 95 °C for 5 hours. After drying, the ZnO nanostructures coated oxidized Si sample was annealed at 500 ^oC for 1 hour.

The ZnO nanostructures coated sample was characterized for surface morphologies using scanning electron microscope (SEM) (JOEL JSM6380LA) and atomic force microscope (AFM) (Nanosurf EasyScan 2). The optical properties were measured using photoluminescence (PL) spectrometer (Horiba Jobin Vyon FluoroMax-3) and ultraviolet-visible (UV-Vis) spectroscopy.

3. Results and Discussion

The three-dimensional (3-D) surface morphological behavior of the nanostructured ZnO is demonstrated in the AFM micrograph, given in Figure 2 (a). Figure 2 (b) shows the SEM image of surface morphology of the ZnO nanostructures realized on oxidized Si substrate using precursor concentration of 0.01 M. The flower-shaped and rod-shaped ZnO nanostructures were observed in the SEM image. However, the ZnO nanorods apparently dominate

a

b

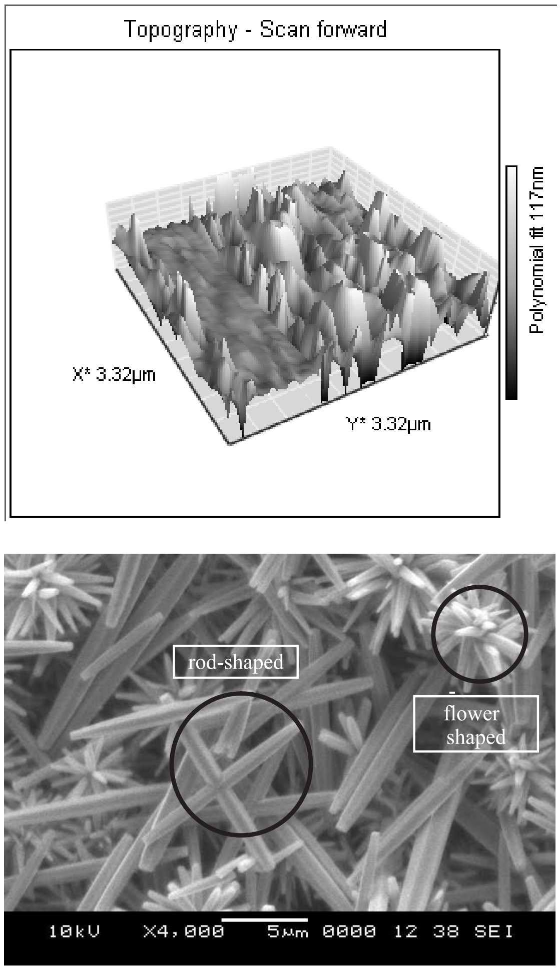

Fig. 2: a) AFM and b) SEM images measured for the ZnO nanostructures.

the surface of the sample. ZnO nanorods with moderate sizes were observed in the SEM image. The diameter of the nanorods is about 600 nm to 1 µm. Besides, the estimated length of the ZnO nanorods is around 5 µm and above.

Photoluminescene spectrum of ZnO nanostructures was measured at room temperature for wavelength ranging from

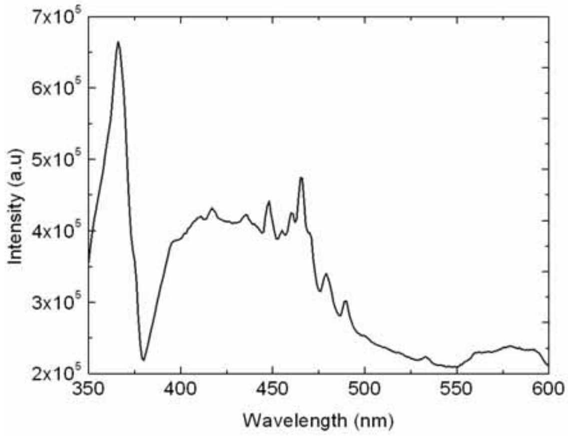

Fig. 3: The room temperature PL spectrum measured for the ZnO nanostructures.

350 nm to 600 nm, as shown in Figure 3. The PL spectrum contains sharp ultraviolet (UV) emission band at approximately 362 nm, which implies that the ZnO nanostructures exhibit high excitation at UV region. It is originated from recombination of exciton corresponding to the near-band gap emission of ZnO /2,5,8/. Figure 3 also shows that the PL spectrum exhibits the broad peak in the visible light range between around 400 nm to 500 nm. The broad band in the visible region is generally believed to associate with the intrinsic defects such as oxygen vacancies, zinc (Zn) interstitials or impurities /5,8,12/.

Figure 4 demonstrates the ultraviolet-visible absorption spectrum measured for the ZnO nanostructures for wavelength ranging from 200 nm to 800 nm. The sample in general has high absorption at UV region (below 400 nm), verifying the presence of the ZnO phases in the realized nanostructures, as shown in PL spetrum.

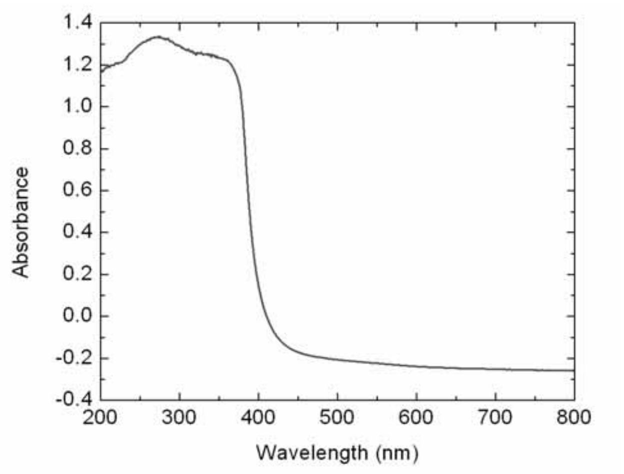

Fig. 4: The UV-Vis spectrum measured for the ZnO nanostructures.

4. Conclusion

ZnO nanostructures have been synthesized using low cost sol-gel hydrothermal technique on oxidized silicon substrates using a precursor's concentration of 0.01 M. The morphological and optical properties of the synthesized ZnO nanostructures were characterized. The scanning electron microscope and atomic force microscope images reveal flower-shaped and rod-shaped ZnO nanostructures, which are confirmed by the photoluminescence (PL) spectrometer and ultraviolet-visible (UV-Vis) spectroscopy measurements. The sol-gel processed ZnO nanostructures are promising material system for many emerging electronic and optoelectronic devices.

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