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Growth of ZnO nanostructures at different temperatures without catalyst by wet thermal oxidation process

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Abstract. In this study, an efficient method to achieve a wide range of high-quality zinc oxide (ZnO) nanostructures through zinc powder evaporation at different temperatures is developed. ZnO nanostructures could be synthesized on n-type silicon substrates by a simple thermal-evaporation technique without a catalyst at 600˚C, 700˚C, 800˚C, and 900˚C. Samples are annealed in wet oxygen and ambient argon gases. Surface morphology, crystallinity, and optical properties of the ZnO nanostructures are examined by scanning electron microscopy and transmission electron microscope measurements, X-ray diffraction, and photoluminescence measurement.

Introduction

As an important wide-band gap semiconductor, ZnO has a direct band gap of 3.37 eV and a high exciton binding energy of 60 meV, which is stronger than that of thermal energy at room temperature. It has a stable wurtzite structure with lattice parameters of a=0.325 nm and c=0.521 nm. One- dimensional ZnO nanostructures could be synthesized using various methods. Many techniques have been successfully used to synthesize ZnO nanowires, including vapor–liquid–solid (VLS), thermal-evaporation and condensation by vapor–solid (VS), and solution-based growth techniques [1–3]. In recent years, ZnO nanostructures grown on Si-based substrates have been receiving increased interest due to the main advantages that they offer. To date, extensive research work has been focused on ZnO, which is one of the most useful oxides for optical and sensor applications. Different morphological ZnO nanostructures, including wires [4], belts [5], and rods [6], etc., have been fabricated. Zinc oxide-based material shows attractive properties for different modern technological applications.

This work reports the growth and characterization of high quality ZnO nanostructures on Si (100) substrate at different temperatures (600˚C, 700˚C, 800˚C, and 900˚C). A variety of high-quality ZnO wires, and rods-like nanostructures have been synthesized using wet thermal oxidation process under vapor-solid (VS) technique without catalyst.

Materials and Methodology

In this project, the synthesis process was carried out in a controllable tube furnace with a quartz tube (inner diameter, 25 mm). N-type silicon (Si) wafers cut into 12×12 mm^2 pieces with a single polished side were used as substrates. A pure metallic Zn powder (99.9%) as source material was placed into a ceramic boat. The temperature was increased from 400˚C to 600˚C, 700˚C, 800˚C, and 900˚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 1 h to examine the effect of heating temperature on the growth of ZnO nanostructure. The samples were characterized by using scanning electron microscopy (SEM), transmission electron microscope (TEM), high-resolution X-ray diffraction (HR-XRD), and photoluminescence spectroscopy (PL) measurement.

Results & Discussion

The typical morphologies of the synthesized ZnO nanostructures were grown at different temperatures of 600˚C, 700˚C, 800˚C, and 900˚C are shown in Fig. 1. The resulting images of the prepared ZnO depict nanowires and nanorods structures. The diameters of ZnO nanowire grown at 600˚C normally range from 40 to 50 nm, with 3–5 μm length, as seen in Fig. 1(a). After increasing growth temperature to 700˚C, ZnO nanowires formed high-density nanowires, as shown in Fig. 1(c), with measured diameter of approximately 100 nm, and the length of approximately 9 μm. On the other hand, when increased the temperature to 800˚C of the aligned ZnO nanorods were obtained, the average diameter and the length were approximately 250 nm, and 3 μm, respectively. Finally, when increased the temperature to 900˚C, ZnO nanorods with average diameters about 600 nm of the nanorods and the lengths were about 3.5μm was observed. Hence, we find an increase in density, and the diameter of synthesized ZnO nanostructures with the increase in temperatures from 600˚C to 900˚C.

In this study, the difference in shapes of nanostructures is considered originated from different growth mechanisms under various temperatures. The mechanism of synthesis one 1D ZnO was based on the thermal evaporation of Zn powders under controlled conditions without the presence of catalyst, different from the ZnO nanowires grown by VLS mechanism. One dimension 1D ZnO nanostructures were formed by oxidation of evaporated zinc vapor in gas phase. It is likely that the growth was governed by a vapour–solid process. Also the difference in shapes of nanowires is considered originated from different growth mechanisms under various temperatures.

During the heating process from 600˚C to 900˚C ZnO wire-like nanostructures and nanorods had been observed. The growth mechanism of ZnO nanowires needs nucleation sites as templates to start along a preferential direction. These nucleation sites were likely to be shaped from the Zn atoms were continuously evaporated from the Zn powder, but the main reaction probably occurs between Zn vapour and the absorbed water vapor rather than O_2, this suggests that the formation of ZnO nanowires is directly related to Zn–H_2O reaction rate.

Furthermore, the growth of ZnO nanowires at these temperatures (600˚C-700˚C) were slightly higher than the melting point of metal zinc 419˚C, so that a small amount of zinc gas was transported to the substrate surface. Since of low reaction activity, the Zn atoms can only stay on the substrate with forming a liquid Zn or ZnOx (zinc suboxides ($x < 1$)) droplets. When this liquid phase saturated with being further oxidised, crystalline ZnO presents. Then, the Zn vapour can be transported or diffused to a low-temperature region (downstream of carrier gas flow), where the Zn vapour is partly oxidized to ZnO or ZnOx ($x < 1$) species again. So, a part of the Zn vapour will condense on the substrate to form liquid droplets, which are the preferred sites to absorb ZnO or ZnOx vapour species. It means that the Zn/ZnO or Zn/ZnOx liquid droplets will be formed and ZnO nanostructures will grow from the supersaturated liquid droplets. This is the nucleation process of nanowires [7].

Subsequently, it had been observed when increased the temperatures from 800˚C to 900˚C more Zn or Zn suboxides vapour were produced. Furthermore, from SEM images it was found if heating temperature increased at these temperatures that indicated is more oxidation so various shapes of nanorod is more likely to form. The vapour condensed on the substrate which might be combining to form bigger nuclei sites for the further growth of nanorods.

The TEM images of ZnO NWs clearly prove that the average diameters of the NWs on Si substrates at (a) 600˚C, (b) 700˚C, (c) 800˚C, and 900˚C as shown on the top right of SEM images Fig.1. TEM images show that ZnO nanostructures have uniform diameter.

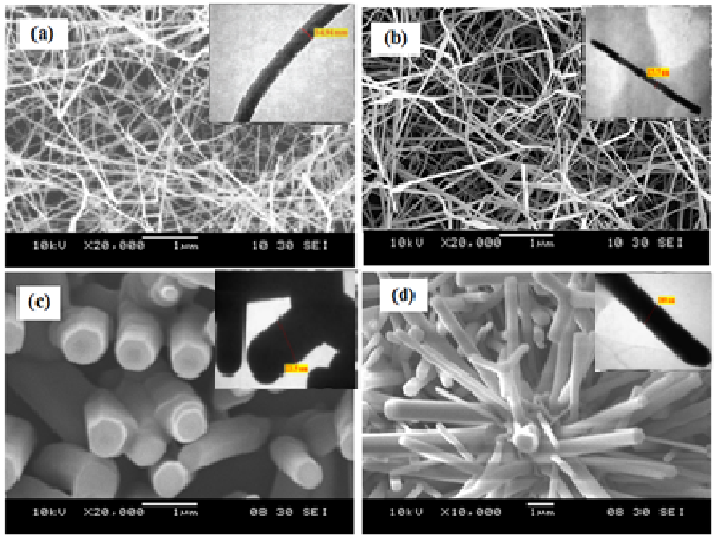

Fig.1: SEM images for ZnO NWs grown on a Si substrate at (a) 600˚C, (b) 700˚C, (c) 800˚C and (d) 900˚C, and the TEM images are inset on the top right of SEM images

The produced samples were examined by HR-XRD to investigate the crystal structure. The XRD pattern of the prepared ZnO nanostructures synthesized from 600˚C to 900˚C is shown in Fig. 2. The diffraction peaks can be indexed to the hexagonal structure of the ZnO according to JCPDS Card No. 01-089-7102. The XRD pattern reveals that the as synthesized layer is polycrystalline. The peaks that appeared at 2Θ of 31.8˚, 34.4˚, and 36.1˚ represent the (1 0 0), (0 0 2), and (1 0 1), phases, respectively, of the hexagonal close-packed crystal structure of the ZnO according to JCPDS no. 36-1451.

The average grain size (D) of the ZnO nanowires (NWs) can be estimated by the Scherrer formula using the full width at half-maximum (FWHM) value from the XRD of (0002) plane. The average value of the size D is about 29, 30, 40, and 42 nm for ZnO NWs grown at 600˚C, 700˚C, 800˚C, and 650˚C, respectively. From the XRD of (0002) plane, also the values of D for the all samples obviously increased with temperature. [Table1] summarizes the peak position of ZnO (0002), the full width at half-maximum, the lattice parameter a and c, and the average grain size for ZnO grown at different temperatures.

Table1: The peak position of ZnO (0002), the full width at half-maximum, the lattice parameter a and c, and the average grain size for ZnO grown at different temperatures.

Sample	Diffraction peak $2\theta_{(0002)}$	FWHM (degree)	Lattice constant $a(nm)$	Lattice constant $c(nm)$	$D(nm)$
600˚C	34.4305	0.2845	0.32531	0.5208	29
700˚C	34.4357	0.26440	0.32552	0.52140	30
800˚C	34.4411	0.19850	0.32526	0.52069	40
900˚C	34.4391	0.18886	0.32531	0.52084	42

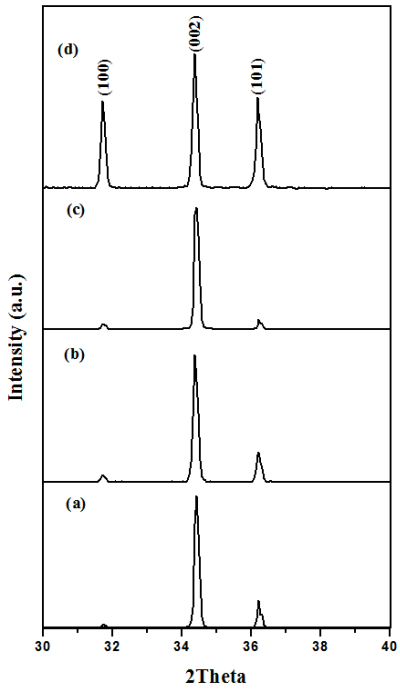

Fig. 2: The XRD pattern of the prepared ZnO NWs (a) at 600˚C (b) 700˚C, 800˚C, and 900˚C.

In addition, it is found from [Table 1] that diffraction angles of (002) peak of all samples is larger than 34.42° of the bulk ZnO [6], implying that the ZnO nanostructures are subjected to a compressive stress in *c*-axis direction. Also the increase of the lattice constant in in-plane of *a* axis and out- plane of *c* axis induced by the tensile stress [8]. These results demonstrate further that there is tensile stress in the ZnO films and that the tensile stress increases as the growth temperature rise.

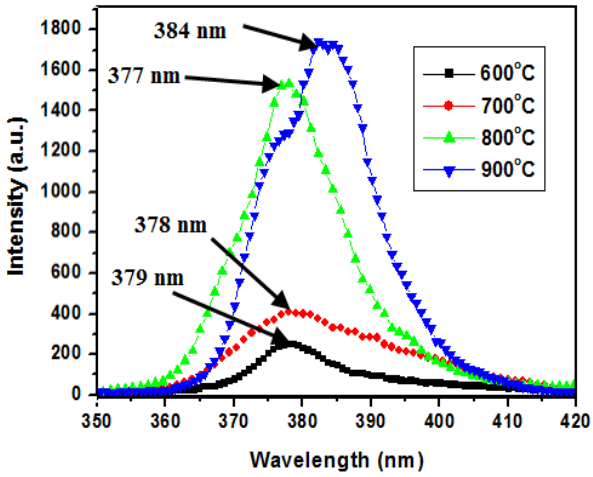

Fig. 3: PL spectra at room temperature of ZnO NWs grown at different temperatures.

Fig. 3 shows the PL spectra of ZnO wires and rod-like nanostructures on Si substrate grown at 600˚C, 700˚C, 800˚C, and 900˚C at room temperature. The peak intensity and peak position of the UV emission were found to be different for ZnO NWs grown at different temperatures. A strong intensity UV peak located at 379 nm, 378 nm, 377 nm, and 384 at 600C˚, 700˚C, 800˚C, and 900˚C, respectively were observed. As a result, the UV peak appearing at 384 nm for ZnO rod-like

nanorods grown at 900˚C exhibited a slight shift towards lower frequency in comparison to the samples. On the other hand, it can be seen the UV peak has more blue shift for the aligned ZnO nanorods grown at 800˚C than that grown at 600˚C, 700˚C, and 900˚C. The large surface area and high optical quality of prepared aligned ZnO nanorods grown at 800˚C make it a suitable material for applications in optoelectronic devices.

The strong UV emission in the PL spectra for all ZnO nanostructures grown from 600˚C to 900˚C indicates that ZnO nanowires had good optical quality. In addition, the slight shift in UV emission was possible because the tensile strain became more intense as the diameter of the ZnO nanostructure increased when the temperature increased [9].

Conclusion

In this study, the structural and optical properties of various ZnO nanostructures grown without catalyst on Si substrates via wet thermal oxidation process are presented. The growth of high quality of ZnO nanostructures at various temperatures was observed. The effect of different temperatures in synthesizing ZnO nanostructures from 600˚C to 900˚C had been analyzed by SEM, TEM, HR-XRD, and PL measurement. It had been obtained that the average diameter of these ZnO nanostructures were increased as a function of temperatures because of the deficiency of oxygen molecules. The deficiency of oxygen molecules had been observed when increased the growth temperature from 600˚C to 700˚C the average length of ZnO nanowires increased as the growth temperatures increased because the amount of oxygen molecules that passed through the Zn vapour decreased, that the diameter of ZnO nanowires decreased as the oxygen flow rate decreased, for this reason the average diameter became smaller and thinner ZnO was obtained when increased the temperatures from 600˚C to 700˚C. Apart from that, it was found that when increased the temperatures from 800˚C to 900˚C that the average length of the nanowires became smaller probably due to shortage of Zn with the same growth time. In addition, the strong UV emission in the PL spectra for all ZnO nanostructures grown from 600˚C to 900˚C indicates that ZnO NWs had good optical quality with the absence of green emission. Therefore, these high-quality nanostructures enrich the family of ZnO nanomaterials and have good potential applications in photodetector, and gas sensors.

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