Chapter 3

Experiment setup

3.1 Introduction

In this chapter, the experimental set up for the growth of zinc oxide nanostructures on Si (100) substrates using carbothermal reaction is presented. In section 3.2, substrate preparations process before ZnO nanostructures growth is discussed. The growth procedure is explained in section 3.3. Doping of ZnO nanostructures with phosphors is reported in section 3.4. Finally, descriptions of various characterization techniques including; field emission scanning electron microscopy (FESEM), energy dispersive x-ray spectroscopy (EDX), high resolution transmission electron microscopy (HRTEM), x-ray diffraction (XRD) and photoluminescence (PL) are explained in section 3.6.

3.2 Substrate preparation

In this study, n-type silicon (100) oriented wafers with the resistivity of 15.5 Ω cm were used as a substrate for ZnO nanostructures growth. The silicon substrate was cut into small pieces (2 cm × 1cm) . To remove contamination of the substrate surface, a chemical cleaning process was applied. This procedure included immersing the substrates at 70°C for 15 minutes in a solution containing a mixture of H_2SO_4 and H_2O_2 in a ratio of 5:1. The substrates were then rinsed in distilled water. After that, the silicon substrates were cleaned in an ultrasonic bath. Finally, the silicon substrates were dried in air. Selections of the cleaned Si substrates were coated with gold using a DC sputtering system. Typical parameters were 10^{-2} torr base pressure, 1500 V plasma voltage, 3.5 mA plasma current and 30 seconds deposition time. The gold-coated silicon substrates were then annealed inside a tube furnace at 700 °C for 30 min under Ar gas at atmospheric pressure.

3.3 Zinc oxide nanostructures growth procedure

For both types of bare and gold-coated substrates, the growth process was preformed in a system consisted of a horizontal tube furnace (30 cm long) with a temperature controller and a gas supply with a control system as shown in Fig. 3.1. The horizontal quartz tube was opened at one end to the air and has the other end linked to a gas supply with a flow rate control system. The source material was a mixture of high-purity ZnO (Sigma Aldrich 99.9%) and carbon powder (Sigma Aldrich 99.95%) with 1:1 mass ratio. A porcelain boat (2 cm in diameter and 8 cm long) with the ZnO/C mixture was placed into the horizontal tube and pushed to the centre of the furnace. Silicon substrate pieces were placed at different locations ranging from 6 to 19 cm downstream from the source material as shown in Fig. 3.2. Deposition of ZnO nanostructures was conducted at

source temperature of 1200°C under 40 standard cubic centimeters per minute (sccm) Ar (99.9%) flow rate for 30 min deposition time. In another test, source temperature was altered from 950 to 1200 °C while, the growth process was performed on a substrate located at 11 cm away from the ZnO:C source (mass ratio of 1:1) under 40 sccm Ar flow rate deposited for 30 min. In order to investigate the effect of Ar flow rate, a mixture of ZnO:C (with 1:1 mass ratio) was heated at 1100 °C for 15 minutes under Ar flow rates ranging from 10 to 70 sccm. Furthermore, the source temperature was held at 1100 °C and the flow rate was 40 sccm, but the deposition time was varied 15, 30, 45 and 60 min for each Si (100). The substrate was located at 11 cm away from the source material ZnO:C (mass ratio of 1:1). In the final test, the ratio of source was varied, i.e., ZnO:C = (2:1), (1:2), (3:1) and (1:3). Each source was put in the centre of the tube where the temperature was kept at 1100 °C for 15 minutes and Ar flow rate of 30 sccm. Table 3.1 summarizes the parameters of the deposition process. The quartz tube was drawn out from the furnace and cooled down to room temperature in the air. White and gray colors products were formed on the surface of the silicon wafers. Using the same experimental procedures, ZnO nanostructures were also grown on gold-coated silicon substrates. According to the furnace manual, the temperature inside the furnace was uniform in the region 7.5 cm away from the centre, after that it should dramatically decreased downstream as shown in Fig. 3.2 [120].

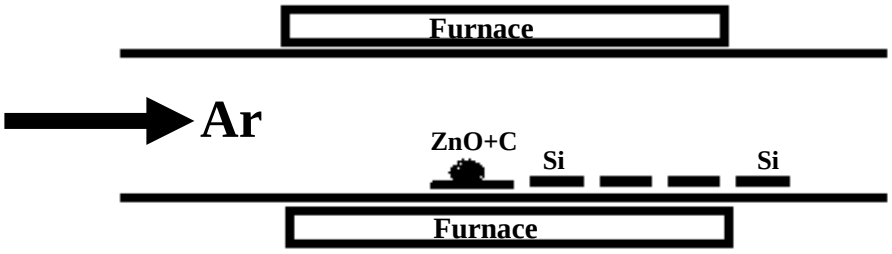

Fig. 3.1. A schematic diagram of the experiment setup used in the growth process.

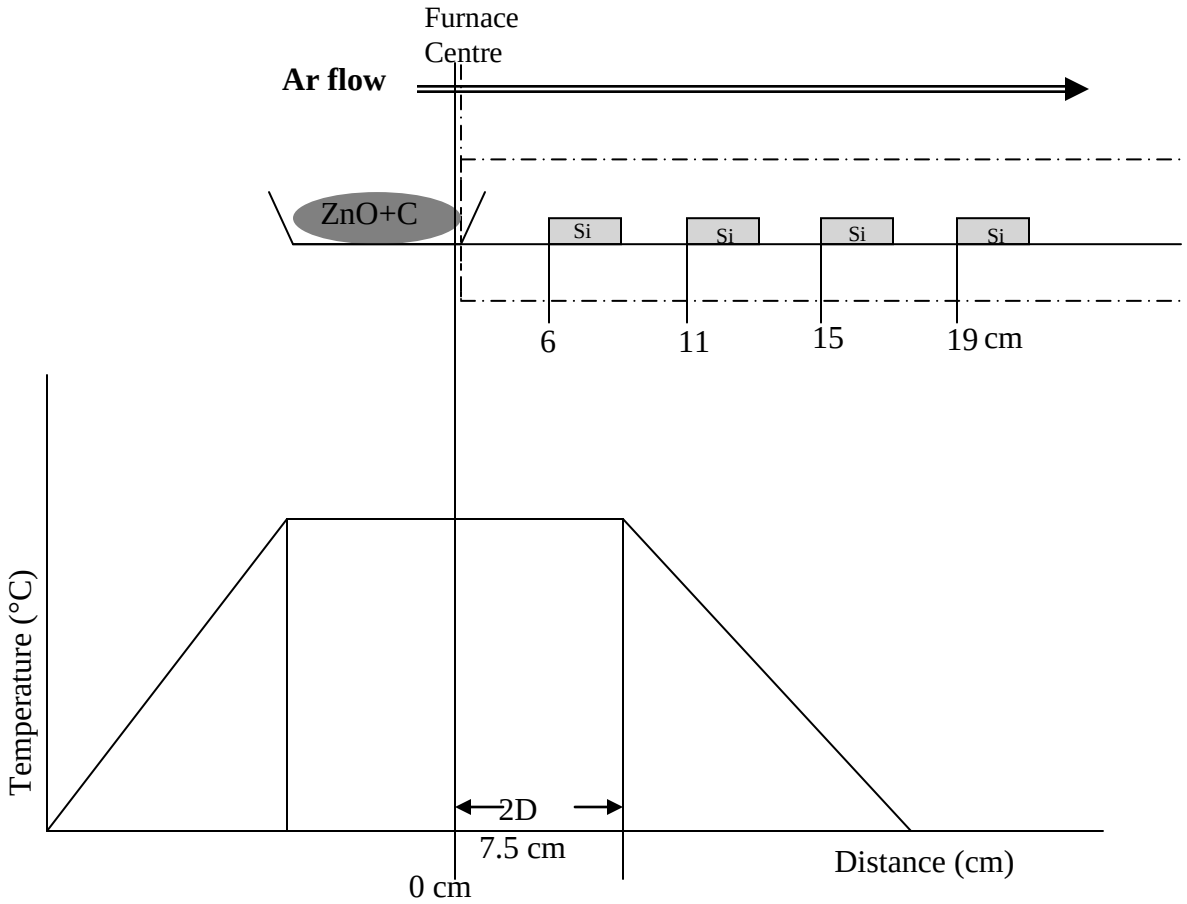

Fig. 3.2. The positions of silicon substrates downstream the source material inside the tube furnace (upper graph) and the uniformity curve temperature zone inside the tube furnace.

Table 3.1. The growth parameters used in this work.

Experiment Number	Source temperature (°C)	Ar flow rate (sccm)	ZnO:C ratio	Deposition time (min)	Distance of substrate from source(cm)
1	1200	40	1:1	30	6, 11, 15 and 19
2	1200, 1100, 1000 and 950	40	1:1	30	11
3	1100	10, 30, 50 and 70	1:1	15	11
4	1100	40	1:1	15, 30, 45 and 60	11
5	1100	30	(2:1), (1:2), (3:1) and (1:3)	15	11

3.4 Doping of ZnO nanostructures

In the typical growth process, ZnO:P nanostructures have been synthesized by the same system illustrated in section 3.3. A mixture of high-purity ZnO powder (Sigma Aldrich 99.9%), graphite powder (Sigma Aldrich 99.95%) and P_2O_5 powder with 1:1:1 mass ratio was used as the source. The source material was loaded in a porcelain boat (2 cm in diameter and 8 cm long) and was set at the centre of the tube furnace. Si(100) substrate was cleaned using a standard wafer cleaning procedure and set to a fixed distance (11 cm) downstream from the source boat. Argon gas with a total flow rate of 40 sccm was used as a carrier gas. The growth was performed at 1200 °C for 30 min. The quartz tube was drawn out from the furnace and cooled down to room temperature. Brown color products were formed on the surface of the silicon wafers. For comparison, undoped ZnO nanostructures were also produced and the growth procedure for undoped ZnO nanostructures was similar to that of ZnO:P nanostructures, but using a mixture of ZnO and graphite powder only (mass ratio of 1:1).

3.5 Characterization of ZnO nanostructures

The grown ZnO nanostructures were characterized by field emission scanning electron microscopy (FESEM) equipped with energy dispersive x-ray spectroscopy (EDX), x-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM) and photoluminescence (PL).

3.5.1 Field emission scanning electron microscopy (FESEM)

FESEM is a key technique for assessing minimum feature size in nanoscale material research. In this study, FESEM (FEI-Quanta200 FEG) was used to analyze the surface of the substrates after growth process. The resolution of FESEM is several nanometers. Fig. 3.3 shows an example of FESEM images of ZnO nanostructures on silicon substrate. From FESEM image, the shape and size of the ZnO nanostructures can be obtained. For example, it is clear that ZnO nanostructures shown have hexagonal shapes with 50 nm to 200 nm diameters.

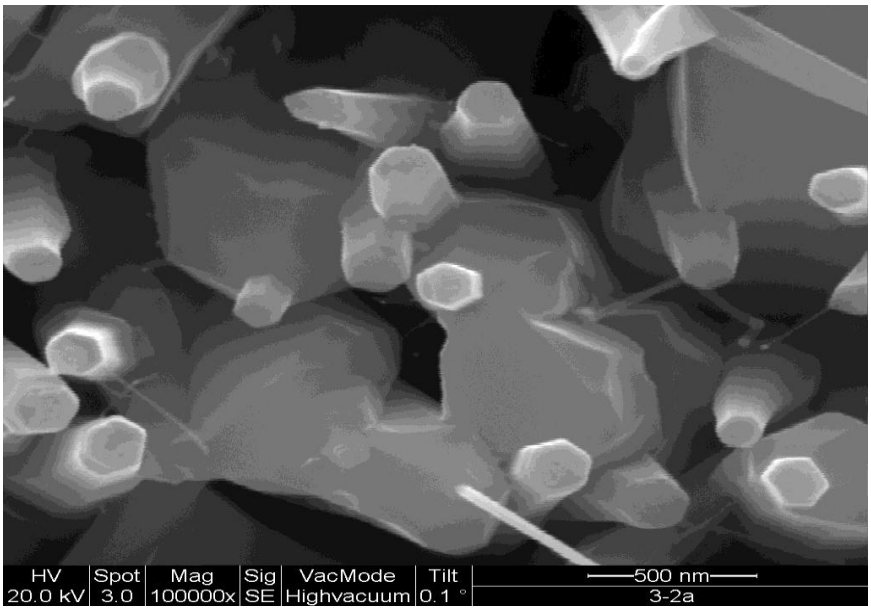

Fig. 3.3. FESEM image of ZnO nanostructures.

In addition, FESEM is equipped with energy dispersive x-ray (EDX) system (Oxford Inca 300) for elemental analysis. Fig. 3.4 shows an example of EDX spectrum of ZnO nanostructures fabricated on silicon substrate. The result showed that the nanostructures were composed of zinc and oxygen; confirming that the nanostructures are ZnO. The Si peak is coming from silicon substrate.

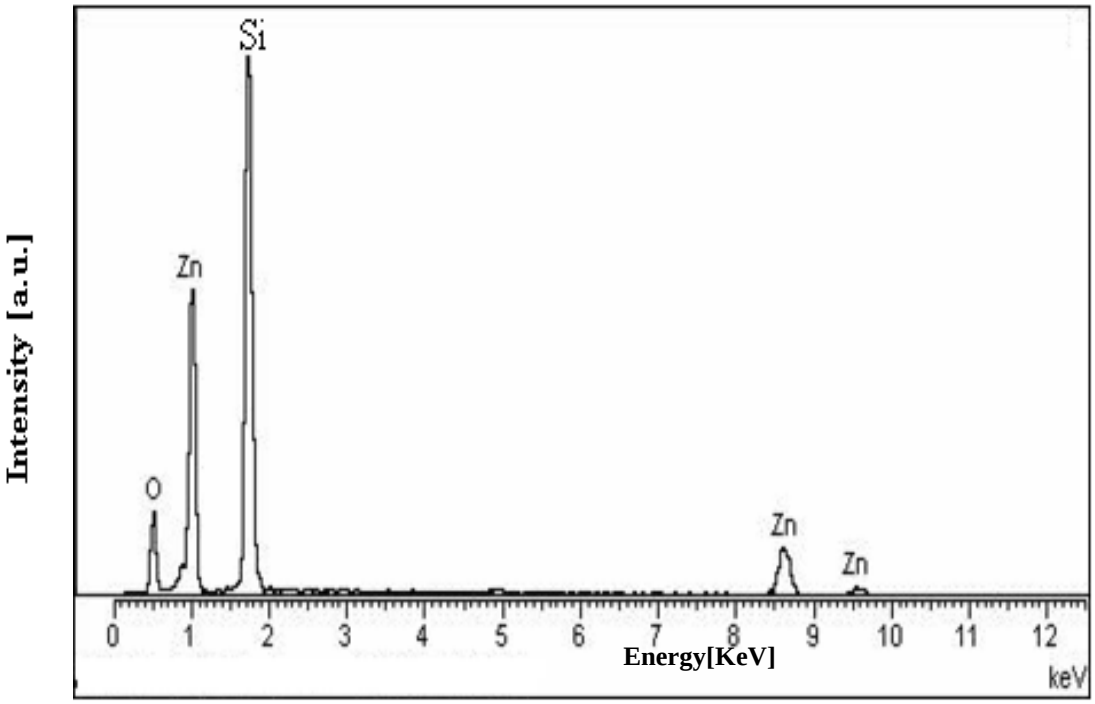

Fig. 3.4. EDX spectrum of ZnO nanostructures grown on silicon substrate.

3.5.2 X-ray diffraction (XRD)

X-ray diffraction (XRD) is a very important technique that reveals detailed information about the chemical composition and crystallographic structure of the investigated materials. The diffractometer used for the measurements described in this thesis is Siemens D-5000 diffractometer using copper-monochromatized Cu Kα1 x-ray source. The wavelength of the x-ray is λ=1.540598 Å. The x-ray scans were performed between 2θ values of 30° and 80° with a typical step size of 0.1°. Fig. 3.5 demonstrates XRD pattern of ZnO nanostructures grown on gold-coated silicon substrate.

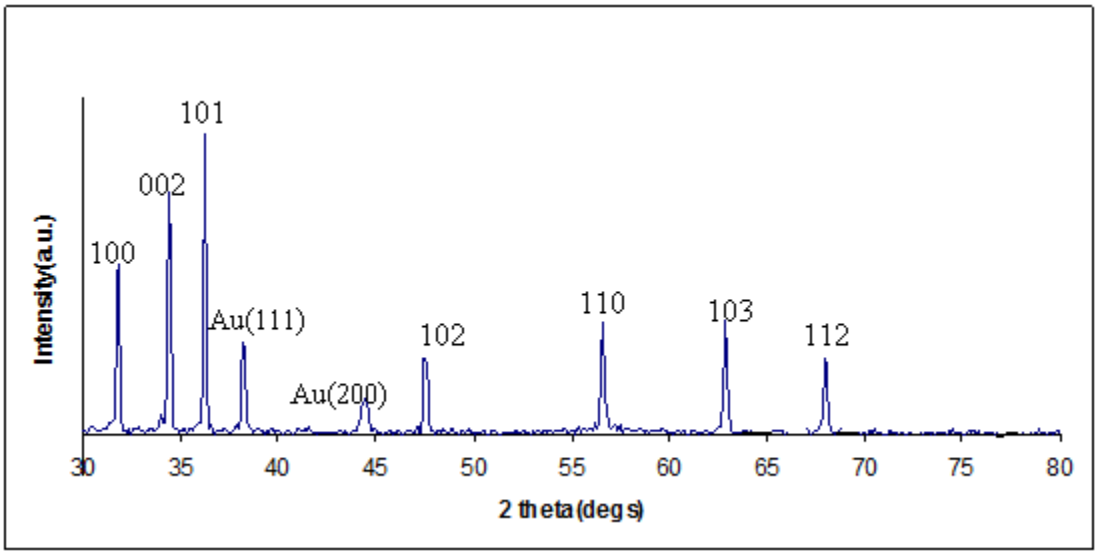

Fig. 3.5. XRD pattern of ZnO nanostructures grown on gold-coated silicon substrate.

According to Fig. 3.5, the XRD diffraction peaks can be assigned to (100), (002), (101), (102), (110), (103) and (112) standard wurtzite ZnO structure. In addition, Au (111) and Au (200) are corresponding to gold peaks.

The strong intensity and narrow width of ZnO diffraction peaks indicate that the resulting products were of high crystallinity where, more than one diffraction peak appeared on the XRD patterns revealed the polycrystalline nature of the products.

3.5.3 High resolution transmission electron microscopy (HRTEM)

High-resolution transmission electron microscopy (HRTEM) gives information on the size, morphology and the projected crystallographic structure of the investigated specimen. TEM analysis was performed using a JEOL-JEM 2010 microscope at 10–200 kV. Figure 3.6 shows the structure of ZnO, which is a wire shape and of a uniform diameter. Moreover, HRTEM image shows the arrangement of atoms inside the nanowires, with the bright points being the interspaces inside the crystal and the dark thread being the shadow of the atom inside the crystal.

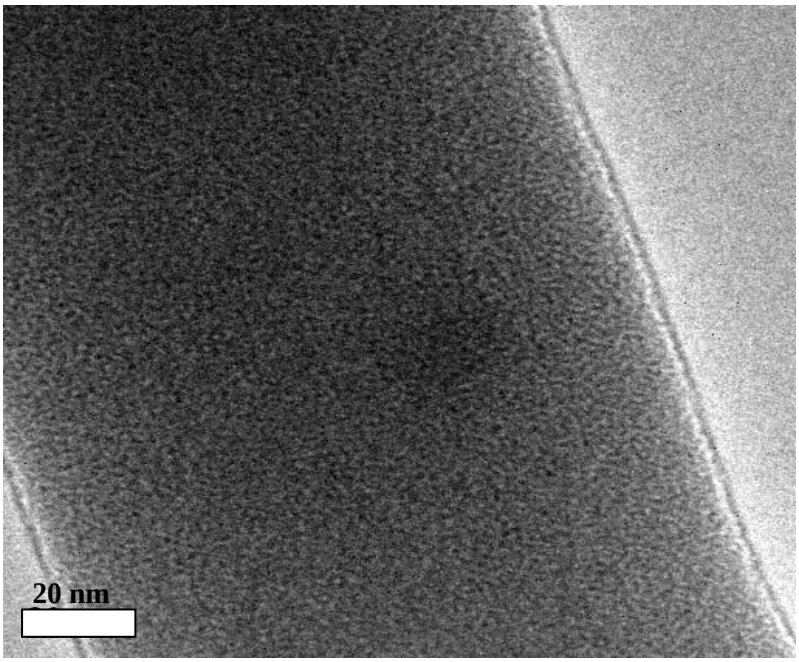

Fig. 3.6. HRTEM image of ZnO nanowire.

3.5.4 Photoluminescence (PL)

Photoluminescence (PL) is a result of a spontaneous emission of light from a material under optical excitation. The excitation energy and intensity can be chosen to probe different excitation types and also different parts of the sample. PL investigations can be used to characterize several material properties such as band gap, impurity level and defect recombination, and quality of the material. In this work, PL measurements were performed at the room temperature by using a Jobin Yvon Horiba HR800UV system, where a He-Cd laser (325 nm) was used as an excitation source with the power of 20 mW. The PL spectrum of ZnO nanowires is illustrated in Fig. 3.7 and more details of PL measurements will be discussed in section 4.5.

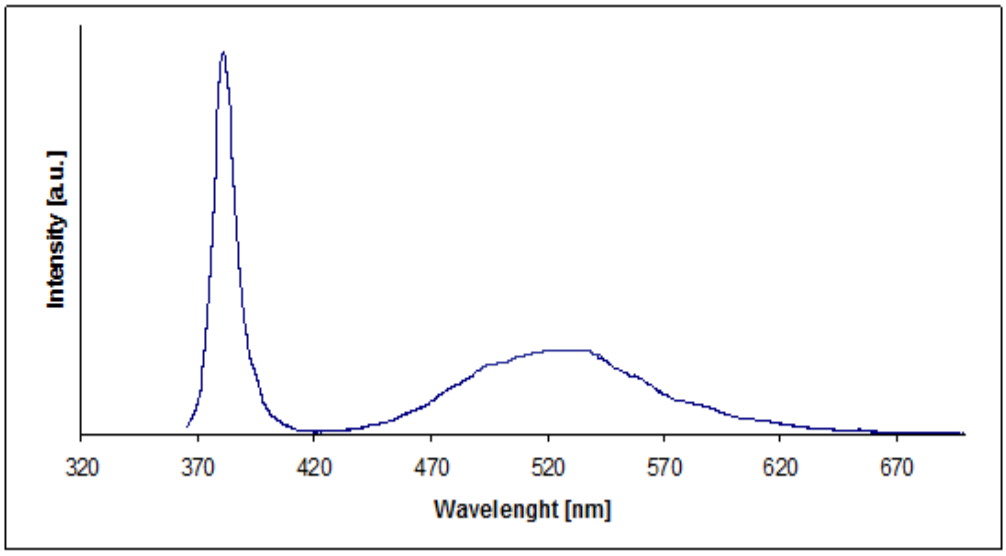

Fig. 3.7. PL spectrum of ZnO nanowires grown on silicon substrate.