Chapter 4

Fabrication and characterization of undoped ZnO nanowires

4.1. Introduction

The exploration of simple, inexpensive, and catalyst-free methods for synthesizing high-quality vertically aligned ZnO nanowires that are grown on silicon substrates has remained a great challenge. In addition, the effect of substrate temperature is an important issue in the thermal evaporation method. This is, because the most important parameter to control the morphological and optical properties of ZnO nanostructures obtained using the physical vapor deposition method is the substrate temperature or substrate position in the tube furnace (Umar et al., 2008; Umar & Hahn, 2008; Yao et al., 2002; Wei et al., 2005; Zhao et al., 2004; Khan & Kordesch, 2005; Zhuo et al., 2008; Li, J et al. 2009). Thus, various amounts of substrate temperatures can lead to ZnO nanostructures with different sizes and shapes. Therefore, if we want to obtain different nanostructure shapes, different temperature zones must be selected for the substrates.

In this portion of thesis the investigation of growth condition effects on the morphological and optical properties of ZnO nanowires will be discussed. In the first step, ZnO nanowires were grown in a conventional thermal evaporation set-up on Si(100) and Si(111) substrates. The effects of different orientations of Si substrates as well as their temperatures on the morphological and optical properties of ZnO nanowires were investigated. In addition, the size effects of ZnO nanowires on the optical properties of ZnO nanowires were studied.
Next, well-aligned ZnO nanowires with different sizes, as well as microdiscs, which were grown on Si (111) substrates using a modified thermal evaporation method, will be discussed. In addition, source temperature effect on morphology of ZnO nanowires will be discussed.

4.2. Experimental details

No metal catalysts, additives, complex procedures, or buffer layers were used in this part of study. Firstly, ZnO were deposited in a conventional horizontal furnace (Fig 3.2). Silicon substrates with (111) and (100) orientations were ultrasonically cleaned with ethanol and de-ionized water, then lightly etched using a mixture of HF (43%) and de-ionized water (1:10) for about 10 minutes to remove the native oxide layer. A mixture of zinc oxide powder (99.99%) and commercial graphite powder in a 1:1 weight ratio was used as the source material. The source material was placed in the center of the furnace and the substrates were located downstream along the tube. High purity nitrogen gas was fed at about 45-55 sccm into the furnace tube at one end, and the other end was connected to a rotary pump. The source material was heated up to 950 °C and the substrates temperatures were varied between 400 and 700 °C. The growth process was allowed to proceed for 1 hour, while a vacuum of 800 Pa was maintained inside the furnace tube during nanowires deposition. Next, ZnO nanowires were grown on Si (111) in a modified set-up with the same conditions, approximately (Fig 3.3). Finally, source temperature in the modified set-up was increased up to 1050 °C.
4.3. Growth and characterization of ZnO nanowires using a conventional thermal evaporation set-up

Figures 4.1(a1-c1) and (a2-c2) show low- and high-magnification FESEM images of some ZnO nanowires deposited on Si(111) at different substrate temperatures (400-700 °C), showing different magnifications for each zone.

Figure 4.1. FESEM images of the ZnO nanowires grown on Si(111) at different temperatures: (a) 700 °C, (b) 550 °C, and (c) 400 °C.
Figures 4.2 show nanowires that were grown on Si (100) at substrate temperatures similar to those shown in Figs. 4.1. As shown, the shapes of the ZnO nanowires vary with the distance from the source material to the substrates. The ZnO nanowires deposited at lower substrate temperatures were denser than those deposited at higher substrate temperatures.

Figure 4.2. FESEM images of the ZnO nanowires grown on Si(100) at different temperatures: (a) 700 °C, (b) 550 °C, and (c) 400 °C.
Different nanowires at different sizes were obtained on substrates in the high and low temperature zones, as supersaturation of the ZnO vapor was different in these zones. Supersaturation plays a key role in the formation of desired morphologies and nanostructure sizes in the thermal evaporation method (Ye et al., 2005).

As no catalyst was used in the growth of ZnO nanowires in this study, the VLS mechanism could not be responsible for their growth. The absence of detectable catalyst particles at the ZnO nanowire tips supports this statement. It appears that the growth of the straight ZnO nanowires reported here occurred via a VS mechanism.

Figures 4.3 (a-b) show the XRD patterns of ZnO nanowires grown on Si(111) and Si(100) under similar substrate temperature conditions. The XRD patterns agree with the standard card for bulk ZnO with a hexagonal structure (JCPDS No. 800075), and no diffraction peaks from other impurities were detected.

![Figure 4.3.](image.png)  
Figure 4.3. (a) XRD patterns of the ZnO nanowires grown on Si(111) at different temperatures. (b) XRD patterns of the ZnO nanowires grown on Si(100) at different temperatures.
Under the same conditions, the XRD results were different for nanowires grown on different orientations of the Si substrate.

PL measurements were used to study the optical properties of the generated ZnO nanowires. Two emission bands appeared in all of the PL spectra of the ZnO nanowires; one was related to UV emission at 375-381 nm and another was related to DLE at 514-517 nm. Figures 4.4 (a₁-c₁) show the PL spectra of the ZnO nanowires deposited on Si(111) substrates at high, medium, and low temperatures, respectively. Figures 4.4 (a₂-c₂) show the PL spectra of the nanowires deposited on Si(100) substrates, using similar temperatures as in Figs. 4.4 (a₁-c₁).

![Figure 4.4. PL spectra of the ZnO nanowires grown on Si(111) at (a₁) 700 °C, (b₁) 550 °C, (c₁), 400 °C and on Si(100) at (a₂) 700 °C, (b₂) 550 °C, and (c₂) 400 °C.](image)

The UV emission intensity relative to the DLE intensity was dependent on both the substrate orientation and substrate temperature. For Si(100) substrates, the UV peak was more prominent in the nanowires that were deposited at low temperatures. On the
other hand, it was more prominent in the nanowires that were deposited at high temperatures on Si(111).

It has been discussed that the presence of DLE peaks is due to defects and O vacancies (Chapter Two). The Si(100) is an appropriate substrate for the growth of ZnO nanowires at low temperatures, as the resulting nanowires have fewer defects than those grown on Si(111); the reverse is true at high temperatures.

The XRD patterns in Figs. 4.3 showed that the preferred orientation of the ZnO nanowires at high temperature zones was (002). Therefore, ZnO nanowires grown in the high temperature zones probably show a c-axis-preferred orientation, namely along [0001]. The lattice mismatch between Si(111) and Si(100) with ZnO(0001) was 13.9% and 39.1%, respectively. Actually, the surface shapes of Si(100) and Si(111) are square and hexagonal, respectively, so the Si(111) plane can present a matched template for ZnO having a hexagonal lattice. As shown in Fig. 4.1(a), the nanowires grown on Si(111) at high temperature were perfectly straight, with a hexagonal shape at their tips. The c-axis of a ZnO nanowire is known to be perpendicular to its hexagonal cross section. Therefore, the orientation of nanowire growth is preferentially along the direction of the c-axis ([0001]) and is characterized by a hexagonal face at the tips.

It has been reported that the kinks in ZnO nanowires may be due to a stacking fault and dislocation, and they may be responsible for the appearance of the green emission in the visible region (Umar et al., 2006). Based on this, the PL spectrum of ZnO nanowires grown on Si(111) at high temperature showed strong UV and weak DLE peaks (Fig. 4.4(a1)). The XRD results from Figs. 4.3 showed that the XRD patterns of ZnO nanowires were grown at 550 °C were approximately the same for two types of nanowires; their PL results were also approximately the same. The ZnO nanowires grown in the low temperature zones were much denser but presented the preferred (101) orientation. These effects could be due to the changing direction of nanowires growth.
with the change in substrate temperature. The temperature and orientation of a substrate are known to be two important parameters that can affect the optical properties of ZnO nanowires when using the thermal evaporation method.

The peak position of the UV emission was dependent on the diameter of the nanowires (Chapter Two). Measurement taken over some nanowires from randomly recorded FESEM images showed that the nanowires were several micrometers in lengths and had an average diameter of 29-75 nm. Figure 5.5 shows the UV emission spectra for various average diameters (29nm ≤ D ≤ 75nm) of nanowires. A blue-shift, from 381 nm to 375 nm, in the peak position of the UV emission, is clearly visible as the diameter of the nanowires decreased.

![UV emission spectra for various nanowires diameters](image)

**Figure 4.5.** UV emission spectra for various nanowires diameters. A blue-shift from 381 to 375 nm in the peak position of the UV emission is clearly visible as the nanowires diameter decreases.

A similar blue-shift in the emission peak in of CL spectra has been observed for a decrease in diameter (120 to 80 nm) of GaN nanorods, as reported by Kim *et al.* (2002). They attributed this energy shift to the surface effect caused by the increasing in
surface-to-volume ratio as the diameter of the nanowires is decreased, as discussed in Chapter Two.

The aspect ratio \((L/D)\) of the nanowires increased with increasing distance between the source material and the substrate. The peak intensities of the UV and DLE emission for six samples were plotted against the nanowires aspect ratio, as shown in Fig. 4.6. The UV emission was more intense in nanowires with small aspect ratios \([(L/D) \leq 300]\), while the DLE emission dominated in nanowires with large aspect ratios \([300 \leq (L/D) \leq 750]\). Nanowires with large diameters tended to have more intense UV emissions. In fact, our results confirmed theoretical method that was discussed in Chapter Two (section 2.2.3.1).

![Figure 4.6. Peak intensities of the UV and DLE emission are plotted against the nanowires aspect ratios. The UV emission was more intense in nanowires with small aspect ratios, while the DLE emission dominated in large aspect ratio nanowires.](image)
4.4. Growth and characterization of ZnO nanowires using a modified thermal evaporation set-up

Figures 4.7 (a₁-c₁) and (a₂-c₂) show low- and high-magnification FESEM images of the ZnO nanowires and microdiscs that were grown on Si(111) substrates.

These were grown on various substrates that were placed at different positions in the furnace: (a) thin nanowires (d ≈ 90 nm) at ~ 650 °C; (b) thick nanowires (d ≈ 300 nm)
at ~ 600 °C; and (c) a mixture of microdiscs with a wide distribution of diameters (800 nm ≤ d ≤ 4 μm) at ~ 550 °C.

The formation of various ZnO nanostructures was only mixed for the sample that was placed the furthest from the source material. Compared with the previous section, the deposition places in the furnace were different (550-650 °C). This could have been due to the change in ZnO vapors concentration in this set-up. Nanostructures with different sizes were also obtained in the different regions of the tube because the supersaturation of ZnO vapor differed in these zones. In addition, under high magnification, as shown in Figs. 4.7(a2-c2), these nano and microstructures appeared to have a perfect hexagonal geometry. Therefore, the orientation of the nanowire and microdiscs growth was preferentially along the c-axis direction ([0001]). A significant difference was found between these results and the nanowires that were grown on Si(111) substrates with the same conditions as in the previous section (Figs.4.1). In fact, we observed that this type of set-up could improve the quality of products when using the thermal evaporation method. Figure 4.8 schematically shows the formation of these nano and microstructures along the tube furnace.

Mensah et al. (2007) used a similar method to grow ZnO nanostructures on silicon substrates coated with Au by controlling the vapor concentration gradients. They have suggested that controlling concentration gradients of ZnO vapors as well as Au vapors could cause the selective growth of pure ZnO nanostructures. On the other hand, in our configuration, only ZnO vapors were responsible for the selective growth of pure ZnO nanostructures. In addition, the diffusion process of ZnO vapors could be affected by Au vapors along the tube furnace; therefore, Mensah et al. (2007) obtained a mixture of different morphologies in all of their samples.
In our set-up, the ZnO nanostructures were grown on catalyst-free substrates. Thus, except for the furthest sample, the samples contained a uniform distribution of ZnO nanowires. One question here is: why did sample (c) contain a variety of microdiscs sizes, while the other samples contained nanowires with approximately uniform sizes? This question could perhaps be answered by Fig. 4.9. The final sample was close to the one-ended tube edge, where a small amount of N\textsubscript{2} gas could have entered into the one-ended tube. The diffusion of N\textsubscript{2} gas could not have occurred much further along the tube due to the tube temperature increase from the edge to the end, which was placed in the center of the furnace (green arrows in Fig. 4.9). Therefore, when ZnO vapors reached the final sample, they were affected by the N\textsubscript{2} gas. This collision between two gases disturbed the flow uniformity of the ZnO vapors in this region. Consequently, the non-uniform ZnO vapors found at this sample site caused the polydispersity growth of ZnO microdiscs. Mensah et al. (2007) suggested that the size of the nucleating nanocrystals, which form at certain locations to relieve strain,
increases with decreasing substrate temperature. At high substrate temperatures, rapid nanowires growth begins immediately after nanocrystals formation, locking in the minimum nanocrystals diameter. For decreasing substrate temperatures, the nanocrystals have more opportunity to grow laterally to distribute strain relief before vertical nanowires or microdiscs begin to grow.

![Diagram of ZnO growth process](image)

**Figure. 4.9.** The green arrows show the diffusion of N\(_2\) gas along the one-ended tube, starting at the edge of the tube. In addition, the size of the green arrows shows the decrease in N\(_2\) gas diffusion along the tube, from the edge to the end of the tube that was placed at the center of the furnace.

Figure 4.10 shows XRD patterns for the ZnO nanowires and microdiscs that were grown in the different temperatures regions: (a) 650 °C, (b) 600 °C, and (c) 550 °C. The XRD patterns in Fig. 4.10 also agree with the standard card for bulk ZnO with a hexagonal structure. No peaks from Zn or other impurities were visible. The dominant (002) peak for samples (a) and (c) indicates that the c-axis of the ZnO nanowires and microdiscs in these samples was perpendicular to the substrate.
Figure. 4.10. XRD patterns for the ZnO nanowires and microdiscs that were grown in different temperatures regions: (a) 650 °C, (b) 600 °C, and (c) 550 °C.

Figure 4.11 shows the room temperature PL spectra of the ZnO nanowires and microdiscs that were grown at different temperatures: (a) 650 °C, (b) 600 °C, and (c) 550 °C. All of the PL spectra showed a strong peak in the UV region at 381 nm and negligible green emission (DLE) peaks at 520 nm in the visible region. Figure. 4.11 shows that the ZnO nanowires and microdiscs had very low concentrations of oxygen vacancies. In fact, the concentrations of the Zn and O vapors could have been increased
in this set-up; in which case; the oxygen vacancy would have been decreased. The ratio of the UV peak to the DLE peak is one of the main factors used for comparing optical properties between samples. The UV/DLE peak ratio increased from sample (a) to sample (c).

![Figure. 4.11. Room temperature PL spectra of the ZnO nanowires and microdiscs that were grown at different temperatures: (a) 650 °C, (b) 600 °C, and (c) 550 °C.](image)

Therefore, the crystallinity of the microdiscs was higher than that of the nanowires. Based on the FESEM results, the average diameter of the ZnO nanostructures increased
from sample (a) to sample (c). In the previous section, we discussed the relationship between the aspect ratio (L/D) of ZnO nanowires and PL emissions. The UV emission was more intense in nanowires with a small aspect ratio, while the DLE emission dominated in nanowires with a large aspect ratio. We suggested that surface effects most likely made a significant contribution to the DLE emission. The results obtained here are in agreement with these previously discussed results. However, due to the larger diameter of nanowires in this step, strong surface effects on band gap of ZnO were not found here, as in the previous results.

A comparison observation between PL results of the two types of nanowires that were grown in the two set-up types, (nanowires were grown at 700 °C in the conventional set-up (Fig. 4.1 (a)) and nanowires were grown at 650 °C in the modified set-up (Fig. 4.7 (a)), is shown in Fig. 4.12.

![Figure 4.12. PL spectra of the ZnO nanowires that were grown in the two types of set-ups.](image)

A significant difference can clearly be seen between these results. The PL spectrum of the nanowires that were grown in the modified set-up shows a larger UV/DLE ratio and smaller full width at half maximum (FWHM) of the UV peaks, in comparison with nanowires grown in the conventional set-up. Therefore, these results confirm that our set-up can indeed improved the crystalline quality and optical properties of ZnO.
nanowires. The diameter size effect of nanowires on the band-gap of ZnO nanowires is also shown again in the inset of Fig. 4.12.

Figure 4.13 shows the Raman spectra of the ZnO nanowires and microdiscs that were grown at different temperatures: (a) 650 °C, (b) 600 °C, and (c) 550 °C. As shown in Fig. 4.13, the Raman spectra of all nanostructures showed an $E_{2\text{H}}$-$E_{1\text{L}}$ peak at 329 cm$^{-1}$ and an $A_{1\text{T}}$ peak at 379 cm$^{-1}$. 436.5-439 cm$^{-1}$ corresponding to the $E_2$(high) mode of the Raman active mode. This is a characteristic peak for the wurtzite hexagonal phase of ZnO. Furthermore, as shown in Fig. 4.13, the FWHM of the $E_2$(high) peak decreased from sample (a) to sample (c). Therefore, these results and the PL results show that the crystallinity of the microdiscs was higher than that of the nanowires. Figure 4.13 (a) shows an additional peak at 576 cm$^{-1}$ that corresponds to the $E_1$(LO) mode for nanowires grown at 650 °C. Therefore, the appearance of the $E_1$(LO) mode for sample (a), indicates a lower crystalline quality and a higher oxygen vacancy for the ZnO nanowires grown on the substrates in a 650 °C environment, in comparison with the other nanostructures. Therefore, the Raman results also confirm that surface effects are very important factor in the quality of nanostructures with smaller sizes.
Figure 4.13. Raman spectra of the ZnO nanowires and microdiscs that were grown at different temperatures: (a) 650 °C, (b) 600 °C, and (c) 550 °C.
4.4.1. Source temperature effect on morphological properties of ZnO nanowires grown using a modified thermal evaporation set-up

In the previous section (section 4.4), the effects of substrate position on the morphological properties of nanostructures grown in a modified thermal evaporation set-up were described. In this section, the effects of the source temperature on the morphological properties of nanostructures are discussed. Therefore, the source material was heated up to 1050 °C, while Si(111) substrate was placed at 650 °C.

Figures 4.14 (a) and (b) show FESEM images of the ZnO nanowires that were grown at source temperature of 950 and 1050 °C, respectively. As shown, a significant difference between the shapes of nanowires was found for these different temperatures. Figure 4.14 (a) shows semi-aligned and vertical nanowires with hexagonal shapes at their tips, for nanowires that were grown at a source temperature at 950 °C. On the other hand, Fig. 4.14 (b) shows non-aligned nanowires with spear shapes at their tips for nanowires that were grown at a source temperature of 1050 °C. Both types of nanowires exhibited approximately the same average diameter (≈ approximately 85 nm) and aspect ratio (L/D). Based on the previous discussion, the growth direction of the hexagonal nanowires is [0001].

![Figure 4.14. (a) FESEM image of ZnO nanowires with hexagonal shapes that were grown at a source temperature of 950 °C. (b) FESEM image of ZnO nanowires with spear shapes that were grown at a source temperature of 1050 °C.](image-url)
Figure 4.15 (a) shows a high-magnification FESEM image of the ZnO nanospears. In addition, a TEM image of a single nanospear is shown in Fig 4.15 (b). As shown in Fig. 4.15 (b), it is clear that the ZnO nanospear is very straight, with an extremely uniform diameter of about 85 nm along its body, a width of about 140 nm at its tip, and a tip angle about 65 °. Figures 4.15 (c) and (d) show the HRTEM image and SAED pattern along the axis of a single nanospear. Both the HRTEM image and SAED pattern strongly suggest that the nanospear has a single-domain wurtzite structure with a high crystal quality. In addition, the HRTEM image shows that the lattice distance was about 0.52 nm, which is consistent with that the distance along the c-axis of bulk wurtzite ZnO crystal. Therefore, based on the HRTEM, the nanospears are also grown along the [0001] direction.

**Figure. 4.15.** (a) High magnification FESEM image of ZnO nanospears. (b) TEM image of a single nanospear. (c) HRTEM image of a single nanospear. (d) SAED pattern of a single nanospear.
As in the previous section, the growth mechanism of these nanostructures can also be discussed by Fick's law. However, one question arises here: why were non-aligned nanospears obtained for sample that was grown at higher source temperature? In fact, the nanospears substrate was further from the source material, in comparison with the nanowires substrate with a hexagonal shape, due to their similar temperatures. Therefore, this substrate was close to the edge of the one-ended tube, where a small amount of N$_2$ gas was able to enter (Fig. 4.9). Therefore, when the ZnO vapors reached this substrate, they were affected by the N$_2$ gas. This collision between two gases disturbed this flow uniformity of the ZnO vapors in this region. Consequently, the non-uniform ZnO vapors found at this sample caused the growth of non-aligned ZnO nanowires. In addition, the spear shape of these nanowires may have been due to this effect. One of the main parameters that is important for obtaining different morphologies is the volume of oxygen in a chamber (Wang, X et al., 2007; Ye et al., 2007). The ZnO powder was the only oxygen source in this set-up. The higher source temperature and carbon in the source caused more ZnO powder to transfer into Zn vapor and O$_2$ gas. Therefore, the interaction between N$_2$ and O$_2$ gases close to the tube edge forced some of the O$_2$ gas back into the one-ended chamber, owing to its lighter mass compared with Zn.

Figure 4.16 shows XRD patterns for the ZnO nanostructures. The XRD patterns in Fig. 4.16 also agree with the standard card of bulk ZnO with a hexagonal structure. No peaks from Zn or other impurities were observed.
Figure 4.16. XRD patterns of the hexagonal nanowires and nanospears.

Figure 4.17 shows the room temperature PL spectra of the ZnO nanowires. The PL spectra show strong peaks in the UV region at 381 nm and weak DLE peaks at 520 nm in the visible region for the both samples. The UV/DLE ratio peak of the nanowires with hexagonal shape is bigger than the UV/DLE ratio of the nanospears.

Figure 4.17. PL spectra of the hexagonal nanowires and nanospears. These spectra show demonstrate that the nanospears have lower optical properties than for the hexagonal nanowires.
Figure 4.18 shows the Raman spectra of the ZnO nanowires. Both spectra exhibit a sharp, strong, and dominant peak at 437 cm\(^{-1}\) corresponding to the E\(_2\)(high) mode.

![Raman spectra](image)

**Figure. 4.18.** Raman spectra of the hexagonal nanowires and nanospears. These spectra show that nanospears have a lower crystallinity than for the hexagonal nanowires.

Furthermore, as shown in Fig. 4.18, the FWHM of the E\(_2\)(high) peak for the nanowires with a hexagonal shape is smaller than for the nanospears. In addition, Fig. 4.18 shows a peak at 576 cm\(^{-1}\), corresponding to the E\(_1\)(LO) mode for both types of nanowires. The PL and Raman results demonstrate that crystallinity and optical properties of the nanospears are lower than for the hexagonal nanowires. Thus, these results are further evidence for our claim that the nanospears have higher oxygen vacancies due to the interaction between oxygen and nitrogen gases.