

Synthesis and photoluminescence studies on ZnO nanowires

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Abstract

ZnO nanowires were grown in gram quantities on graphite flakes (as collector) using the vapour transport and condensation approach. The yield, defined as the weight ratio of ZnO nanowires to the original graphite flakes, has been studied thoroughly by tuning the various growth parameters such as pressure and temperature inside the tube furnace, the amount of graphite powder in the original source, the source to collector ratio, etc. A yield as high as 200% has been achieved, equivalent to a 40% conversion of the ZnO powder in the original source. A study comparing the photoluminescence spectra of the ZnO nanowires grown on both graphite flakes and substrates with commercially available ZnO powder has been carried out.

1. Introduction

Zinc oxide (ZnO), a large band-gap (3.37 eV) semiconductor, is a potentially important material for laser diodes and light emitting diodes [1], optical waveguides [2, 3], optical switches [4, 5], transparent ultraviolet (UV) protection conducting film [6, 7], and acousto-optic [8] and surface acoustic applications [9]. At the same time, high exciton binding energy (60 meV) makes it a promising candidate for room temperature ultraviolet laser diodes [10, 11]. Furthermore, ZnO has been well-studied as a sensor material [12, 13]. It also has been demonstrated for applications in solar cell [14], photo-catalysts [15], etc. One-dimensional ZnO nanowires have a lower threshold lasing-energy due to quantum effects. This results in a substantial density of states near band-edges and enhances radiative recombination due to carrier confinement [16], which leads to many optical and opto-electronic applications [16–18]. The naturally high surface-to-volume ratio of quasi-one-dimensional nanowires has made it a contender for chemical and biological sensors [19, 20]. In order to explore these applications, a full understanding of the growth and availability of large quantities is needed. In the past two years, several research groups have claimed success in

producing ZnO nanowires by chemical vapour deposition (CVD) [21, 22], metal organic chemical vapour deposition (MOCVD) [23, 24], physical vapour deposition (PVD) [25], thermal evaporation [26], etc. However, none of the reports was about production of gram quantities. Recently, we succeeded in producing gram quantities of freestanding, ZnO nanowires [27] by vaporizing a mixture of ZnO and graphite powder at 1000–1200 °C in a tube furnace followed by condensation on micron-sized graphite flakes at a pressure of 1–2 Torr air. In this paper, we describe the details of yield-control by parameters such as pressure, temperature, source (mixture of ZnO and graphite powder)-to-collector (graphite flakes) ratio, etc. We also report a detailed study on photoluminescence spectra of the ZnO nanowires in comparison with those of commercial ZnO powder.

2. Experimental details

ZnO powder (Alfa Aesar, 99.9%) and graphite powder (Alfa Aesar, 99.9%) were mixed well in varying atomic ratios and placed in one end of a quartz boat as the source. In the same boat, graphite flakes (Pennsylvania Micronics) were spread uniformly about 2–3 cm from the source along the direction of airflow in order to collect the nanowires. The entire boat was covered by a quartz plate. A small opening was left to facilitate airflow into the assembly. The complete unit was placed into

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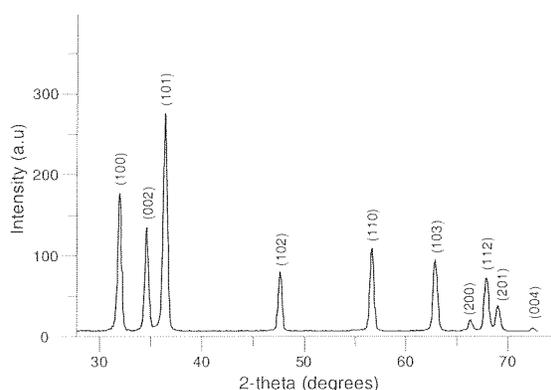


Figure 1. XRD pattern of oxidized freestanding ZnO nanowires.

the horizontal ceramic tube of a high temperature furnace with a sharp temperature gradient. In order to maintain a desired pressure from 0.1 to 10 Torr air, one end of the ceramic tube was connected to a rotary pump while the other end was sealed with a silicone stopper equipped with a needle valve. The furnace was heated to 900–1100 °C at a rate of 60–80 °C min⁻¹ and kept at that temperature for 10–75 min. The boat was positioned inside the furnace in such a way that the source was at 1000–1100 °C and the graphite flakes at 700–900 °C. After cooling down to room temperature, the original black graphite flakes turned grey in colour, indicating that a significant amount of ZnO had been deposited onto the graphite flakes.

In order to remove the graphite flakes, the as-made samples were placed in another horizontal quartz tube of a tube furnace and oxidized at 700 °C for about 2 h under flowing O₂ gas. After oxidation, the sample turned white, indicating the removal of graphite flakes. Oxidation decreases the electrical conductivity due to oxygen over-doping. To restore the conductivity, the nanowires were reduced either in a vacuum and then flowing H₂, or in flowing H₂ only. The reduction was normally carried out at 400–500 °C for 1 h.

The morphology and the structure characterization was conducted using scanning electron microscopy (SEM, JEOL-6340F), transmission electron microscopy (TEM, JEOL-2010F), and Bruker-AXS x-ray diffractometry (G8 GADDS). Photoluminescence (PL) studies were performed at room temperature using a dual-scanning micro-plate spectrofluorimeter (Molecular Devices Inc., SpectraMax Gemini XS) with excitation at 325 nm.

3. Results and discussion

X-ray diffraction (XRD) examination of the samples resulted in similar patterns as shown in figure 1, indicating that the nanowires are highly crystallized. The diffraction patterns were indexed to a typical wurtzite structure with unit cell constants of $a = 3.248 \text{ \AA}$ and $c = 5.206 \text{ \AA}$.

Typical SEM images of the as-made ZnO nanowires are shown in figure 2. The nanowires generally grow on the exposed surfaces of the graphite flakes. Samples collected from areas close to the source show that the nanowires are longer (8–15 μm) and have smaller diameter (30–50 nm) as shown in figures 2(a)–(d), compared with those far from

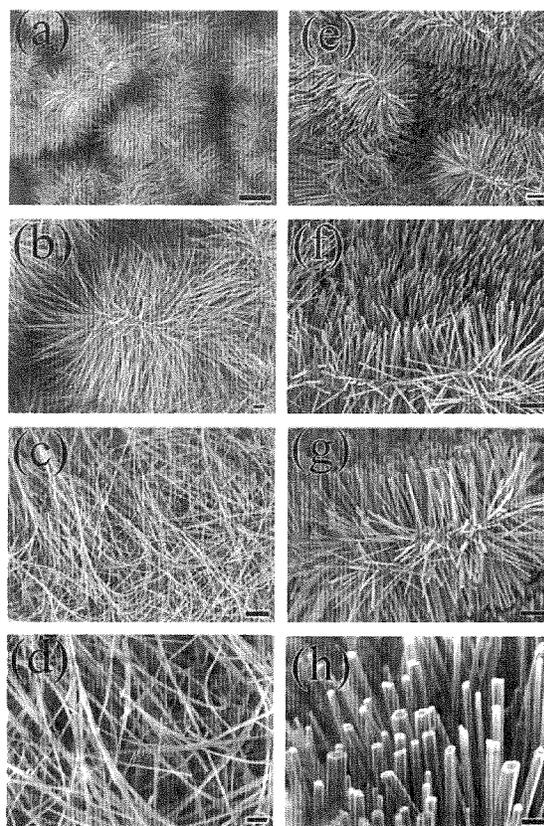


Figure 2. Morphology of as-made ZnO nanowires. (a)–(d) show long (10–15 μm) and thin (30–60 nm) nanowires grown at the higher-temperature region of the furnace. (e)–(h) show short (1–2 μm) and thick (60–100 nm) nanowires grown at the lower-temperature region of the furnace. The scale bar for (a) is 10 μm, for (b), (c), (e), (f), and (g) 1 μm, and for (d) and (h) 200 nm.

the source where the nanowires are shorter (1–2 μm) and have larger diameter (60–100 nm) as shown in figures 2(e)–(h). These shorter and larger nanowires normally have prominent hexagonal structural morphology and are better-aligned perpendicular to the surface of the graphite flakes.

The graphite flakes in the as-made samples can be easily removed from nanowires through an oxidation process. Figure 3(a) shows the SEM image of the freestanding ZnO nanowires after oxidation. Voids due to the removal of graphite flakes can be easily seen. High-resolution TEM (HRTEM) shows that the lattice of the nanowires is perfect. The nanowire growth direction is [0001], and it has a number of (10 $\bar{1}$ 0) facets as shown in figure 3(b). Before oxidation, the nanorods were covered by an amorphous layer of either carbon or turbostratic graphite with thicknesses ranging from a few to 10 nm, as shown in figure 3(c). The amorphous layers were almost completely removed by the same oxidation treatment.

3.1. Pressure dependence

Pressure inside the growth zone determines the amount of oxygen involved in the reaction and the vaporization rate of the source. We varied the pressure from 0.65 to 10 Torr air

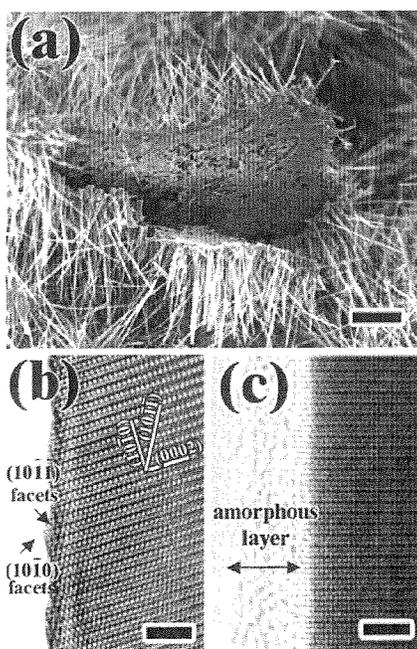


Figure 3. SEM and TEM images of oxidized ZnO nanowires. (a) SEM image showing the voids left by removal of graphite flakes. (b) HRTEM image of an oxidized ZnO nanowire with clean surface. The crystal perfection and atomic arrangement can be clearly seen. (c) TEM image of the surface of an as-made nanowire with an amorphous graphite shell on the surface. The scale bar for (a) is 1 μm and for (b) and (c) 2 nm.

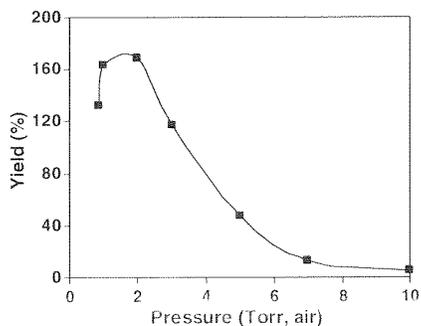


Figure 4. Yield dependence on pressure inside the furnace. The other parameters were: source temperature: 1075 $^{\circ}\text{C}$, collector temperature: $\sim 825^{\circ}\text{C}$, source-to-collector weight ratio: 15:1, Zn to C atomic ratio in the source: 1:4, growth time: 30 min.

inside the tube furnace. Figure 4 shows the yield dependence on the air pressure in the furnace. A maximum yield of around 170% was achieved at 2 Torr. At very low pressure, two things happen:

- (1) fast decomposition of ZnO into ZnO_{1-x} [26, 28] that evaporates and condenses into nanowires,
- (2) short dwelling time of ZnO_{1-x} on the collecting graphite flakes.

Both the fast decomposition and short dwelling time contributed to the low yield. At higher pressure, the oxygen partial pressure is too high to produce enough ZnO_{1-x} . Furthermore,

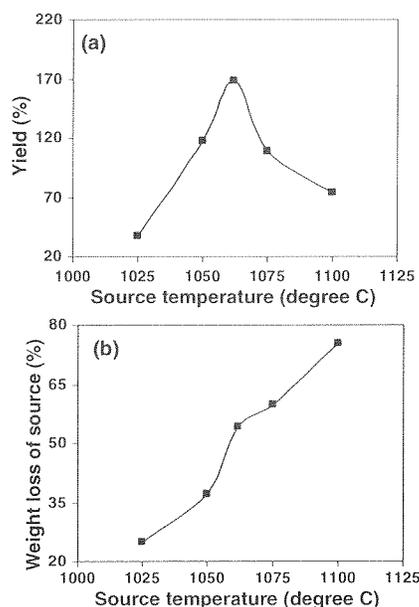


Figure 5. (a) Yield dependence on source temperature. (b) Source weight loss dependence on source temperature. The other parameters were: collector temperature: $\sim 800\text{--}850^{\circ}\text{C}$, pressure inside the furnace: 2 Torr, source-to-collector weight ratio: 15:1, Zn to C atomic ratio in the source: 1:4, growth time: 30 min.

higher pressure generally suppresses the vaporization rate. Both slow production of ZnO_{1-x} and vaporization resulted in low yield at high pressure. It is important to point out that the yield defined here is very conservative since it is assumed that the amount of the collecting graphite flakes did not change during growth. In fact, graphite flakes are slowly consumed due to the presence of oxygen during the growth of ZnO nanowires.

3.2. Temperature dependence

The furnace temperature not only determines the evaporation rate of the source material but also the morphology of the nanowires that are grown. We varied the source temperature from 1025 to 1100 $^{\circ}\text{C}$. Accordingly, the temperature at the collector was between 800 and 850 $^{\circ}\text{C}$. Figure 5(a) shows the yield dependence of the source temperature with a fixed pressure of 2 Torr. A sharp peak around 1060 $^{\circ}\text{C}$ has been observed, suggesting the growth is extremely temperature sensitive. Figure 5(b) shows the weight loss from the initial source. The weight loss is almost linear with temperature, except for a slight up-kink in the middle. This is consistent with the peak in figure 5(a): more vaporization produces more nanowires. It is obvious that the yield increases with source temperature because of a greater supply of vaporized ZnO at higher temperature. Yield decreases when temperature is higher than 1060 $^{\circ}\text{C}$. This is attributed to vaporization, absorption, and diffusion at the initial and growth stages. Obviously, too high a temperature on the collecting graphite flakes will result in slow condensation.

3.3. Source-to-collector ratio dependence

In order to determine how the amount of source affects the yield of ZnO nanowires, we varied the weight ratio of the

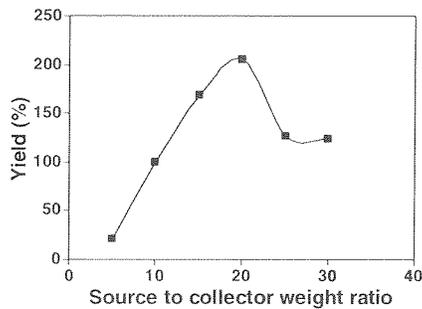


Figure 6. Yield dependence on source-to-collector weight ratio. The other parameters were: source temperature: 1075 °C, collector temperature: 825 °C, pressure inside the furnace: 2 Torr, Zn to C atomic ratio in the source: 1:4, growth time: 30 min.

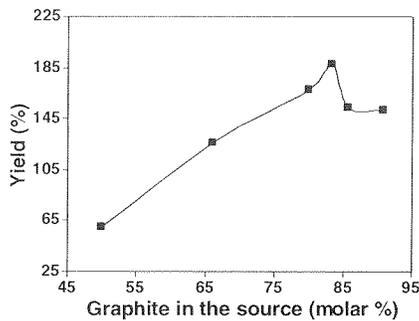


Figure 7. Yield dependence on graphite concentration in source. The other parameters were: source temperature: 1075 °C, collector temperature: 825 °C, pressure inside the furnace: 2 Torr, source-to-collector weight ratio: 15:1, growth time: 30 min.

source to collector from 5:1 to 30:1 while keeping the same atomic ratio of graphite to ZnO (C:Zn = 4:1) in the source. Figure 6 demonstrates the relationship between the yield and the ratio. It is clearly seen that the yield increases with ratio with a maximum of 200% when the weight ratio is 20:1, then decreases. The initial increase is due to the increased vapour supply, whereas the final decrease is because of the shortage of condensation sites from the graphite flakes until they were finally saturated. Therefore, a balance is required between the supply of vapour and sites for growth of the nanowires.

3.4. Dependence of atomic percentage of C content in the source

The amount of graphite powder in the mixed source directly determines the amount of Zn or Zn sub-oxide vapour formed during the evaporation process. We varied the relative amount of graphite to ZnO from 50% (atomic ratio C:Zn = 1:1) to 90% (C:Zn = 10:1). The weight ratio of source to collector was kept at 15:1. Figure 7 shows the yield dependence of the source composition. A maximum yield of around 190% has been achieved with 83% (C:Zn = 5:1) graphite in the source. It is understood that graphite in the mixed source reacts with both ZnO and oxygen to form either CO₂ or CO. The formation of CO is crucial to the formation of Zn and Zn sub-oxide vapour [26]. A higher graphite concentration will obviously produce more nanowires due to a greater supply of ZnO_{1-x}

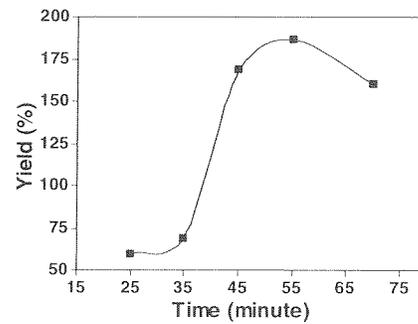


Figure 8. Yield dependence on growth time. The other parameters were: source temperature: 1075 °C, collector temperature: 825 °C, pressure inside the furnace: 2 Torr, Zn to C atomic ratio in the source: 1:4, source-to-collector weight ratio: 15:1.

vapour. On the other hand, too much graphite in the source reduces the amount of ZnO, leading to a decrease in nanowire formation and eventual saturation.

3.5. Dependence on reaction time

We also varied the reaction time from 10 to 75 min to see if it plays an important role in yield (only data from 25 to 70 min are presented). Figure 8 shows the yield dependence on time. Obviously, a longer reaction time produces longer and more numerous nanowires. However, if the reaction time is too long, the yield does not increase further simply because of the depletion of the ZnO source. Furthermore, a reaction time that is too long also provides the conditions for nanowire evaporation. This is illustrated by the fact that shortening and thinning of the nanowires is observed for nanowires near the source due to the reaction of graphite with nanowires (images not shown).

4. Photoluminescence results

Photoluminescence (PL) of nanowires grown on graphite flakes was studied in comparison with commercial ZnO powder using a dual-scanning micro-plate spectrofluorimeter with excitation frequency 325 nm at room temperature. A reduced, near band-edge (NBE) ultraviolet (UV) peak and a prominent deep-band green peak around 520 nm was observed. It is generally accepted that the surface states play a crucial role in PL spectra of nanomaterials [29]. The green peak of ZnO is due to radiative recombination of a photo-generated hole with an electron attributed to an oxygen vacancy [29]. So the amount of oxygen in the surface is expected to drastically change the green-band peak. The UV peak at room temperature is attributed to an NBE free exciton transition, namely the recombination of a free exciton through an exciton–exciton collision. It has been suggested that high crystallinity (decrease of impurity and structural defects such as oxygen vacancy, dislocations etc) and the diameter of the nanowires play key roles in the enhancement of NBE emission [21, 30, 31]. Our high-resolution TEM images show that the nanowires are highly crystalline and free from impurity or dislocations. Figure 9(a) shows the variation of the green-peak intensity of ZnO nanowires processed under different conditions. The as-made ZnO nanowires have been

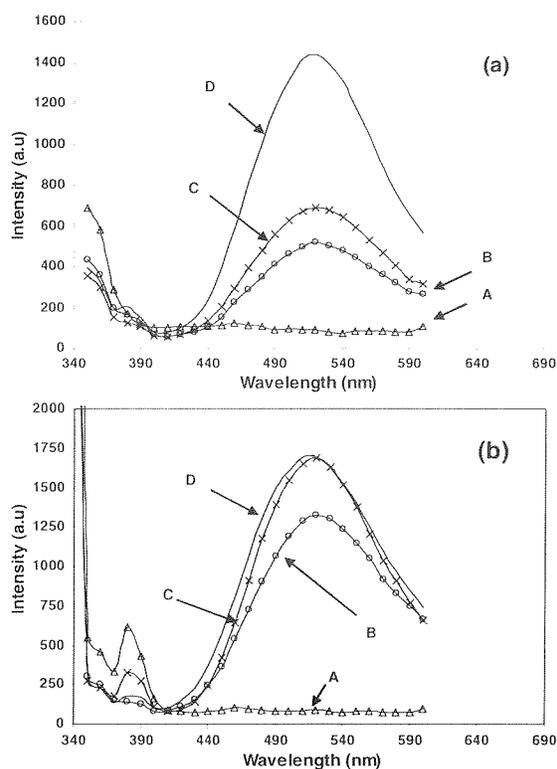


Figure 9. Photoluminescence spectra of ZnO nanowires and powder. (a) PL spectra of ZnO nanowires; plot A: as-made nanowires, B: oxidized nanowires, C: oxidized and then vacuum annealed nanowires, D: oxidized, vacuum annealed, and then H_2 annealed nanowires. (b) PL spectra of commercial ZnO powder mixed with graphite powder processed at various annealing conditions; plot A: mixture of ZnO and graphite powder, B: after oxidation of A, C: after oxidation and vacuum annealing of A, and D: after oxidation, vacuum annealing, and H_2 annealing of A.

oxidized for 2 h in flowing O_2 , and then annealed in vacuum for 2 h and finally in flowing H_2 for 1 h under 1 Torr pressure. The subsequent decrease of the oxygen content caused by annealing manifests itself in a subsequent increase of the green-band peak. As shown in figure 9(a), the UV peak intensity for ZnO nanowires does not depend significantly on these processing conditions except for the H_2 annealed sample. A similar dependence of green-band intensity on processing conditions was also observed on a mixture of commercial ZnO and graphite powder as shown in figure 9(b). H_2 annealing was observed to be more effective in increasing the green peak for nanowires than for samples containing a mixture of micro-sized ZnO and graphite powder. We believe that this originates from a higher surface-to-volume ratio for the thinner nanowires, resulting in more surface and sub-surface oxygen vacancies. Unlike the green-band transitions, the UV peak intensity behaves differently under the same processing conditions. The mixture has few oxygen vacancies before heat treatment and exhibits an intense UV peak as expected. Suppression of the UV peak after annealing in H_2 compared to vacuum is probably due to the creation of surface defects.

To find out why the UV peak is suppressed and whether the graphite flakes play any role, we compared photoluminescence

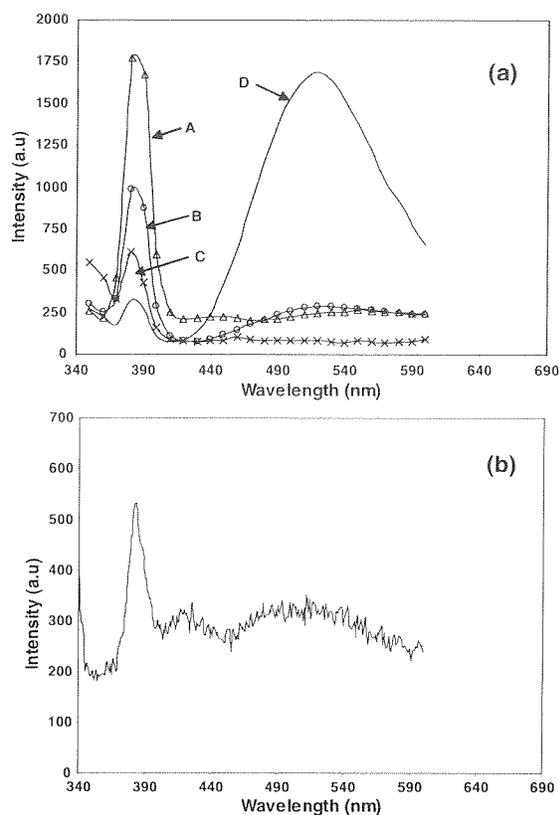


Figure 10. (a) PL spectra of commercial ZnO powder processed at various conditions; plot A: commercial ZnO powder, B: mixture of ZnO and graphite powder, C: after oxidation and vacuum annealing of A, D: after oxidation and vacuum annealing of the mixture of B. (b) PL spectra of the ZnO nanowires grown on a sapphire substrate.

spectra between oxidized samples of commercial ZnO powder and a mixture of ZnO and graphite powder. The result is demonstrated in figure 10(a). It is evident that mixing of graphite not only reduces the NBE emission but also enhances the deep-level green-band emission. To further confirm it, we grew ZnO nanowires on sapphire substrates (without graphite flakes). As-made ZnO nanowires grown on sapphire substrates exhibit a prominent UV peak at about 383 nm with a very weak, deep-band, green peak as shown in figure 10(b). So, one can assume that the as-made nanowires have a low concentration of oxygen vacancies. It can be concluded that the graphite in ZnO induces oxygen vacancies during annealing, which enhances the deep-level to near band-edge emission ratio.

5. Conclusions

In conclusion, gram quantity, high quality ZnO nanowires have been successfully synthesized on micron-sized graphite flakes by the vapour transport and condensation method. The various growth parameters have been thoroughly studied to control yield. The yield of the nanowires has been shown to reach 200%. PL spectra of the samples have been studied. It was found that the presence of graphite in as-made nanowires causes suppression of the UV peak and enhances the deep-level green-band peak after oxidation.

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