

Influence of Growth Temperature on the Photoluminescence of Zinc Oxide Nanomaterial

Alvin Noe Ladines, Gil Nonato Santos

Abstract— We report the synthesis of zinc oxide nanomaterials on glass substrate through the non-catalytic horizontal vapor phase growth method. The optimal growth conditions in the growth of a particular kind of nanomaterial were determined. Nanobelts with average width of 200 nm were grown when the growth temperature was set at 1200°C and 1000°C. Nanowires with mean diameter of 100 nm were dominant at growth temperatures of 800°C and 600°C. Shorter growth time resulted in the formation of needle-like structures which are 2 micrometers in length. Increasing the growth time corresponded to the growth of nanowires with average length of 10 micrometers. XRD measurements showed that the synthesized nanostructures have a hexagonal wurtzite structure with growth preference in the (001), (101) and (10-1) directions. The room-temperature photoluminescence spectra showed an intense ultraviolet emission (UV) at 3.26 eV with weak emissions in the visible light regime. The strong UV emission can be attributed to the recombination of free excitons through an exciton-exciton collision process. Meanwhile, the deep level emissions are caused by oxygen vacancies in ZnO and the emission results in the recombination of the photogenerated hole with an electron occupying the oxygen vacancy. It is proposed that growth mechanism involved in the formation of ZnO nanostructures is the vapor-solid process because no catalyst was used.

Index Terms— nanomaterials, photoluminescence, scanning electron microscopy, thermal evaporation, vapor-solid growth, X-ray diffraction, zinc oxide

1 INTRODUCTION

RECENTLY, there has been a growing interest in zinc oxide nanomaterials because of their excellent optoelectronic [1], piezoelectric [2], gas sensing [3] and lasing properties [4]. Different nanostructures of ZnO including nanowires, nanobelts, nanohelices, nanocages, needle-like and comb-like structures can be synthesized through various methods reported in literature. The noncentral wurtzite crystal structure of ZnO and the tetrahedrally coordinated ZnO₄ unit result in its anisotropic piezoelectric properties. Rapid growth in the <0001>, <0110> and <2110> directions and polar surface-induced phenomena result in the formation of the diverse group of nanostructures of ZnO. [5]

ZnO is a wide band gap semiconductor with a direct band gap of 3.36 eV and a large excitation binding energy of 60 meV thus exhibiting near-ultraviolet emission and transparent conductivity. Also, ZnO is biologically-safe and biocompatible so it can be used for biomedical applications. [4] Various methods were developed to synthesize ZnO nanostructures which includes basic erosion method [6], electrodeposition [7], thermal oxidation [8], vapor epitaxy method [9], chemical vapor deposition [10], vapor-liquid-solid process [11], simple evaporation method [12-14], solution phase reaction [15] and flame synthesis [16] among others.

Horizontal vapor phase crystal growth (HVPCG) method was developed as an economical alternative to the evaporation method. It is a simple and efficient method of growing high purity nanomaterials without using any gas as catalyst. More importantly, it is eco-friendly since the process of evaporation does not interfere with the environment. [17]

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In this paper, we report the synthesis of ZnO nanomaterials through the non-catalytic HVPCG method. The surface morphology, stoichiometry and photoluminescence of the grown nanomaterials will be investigated.

2 PROCEDURE

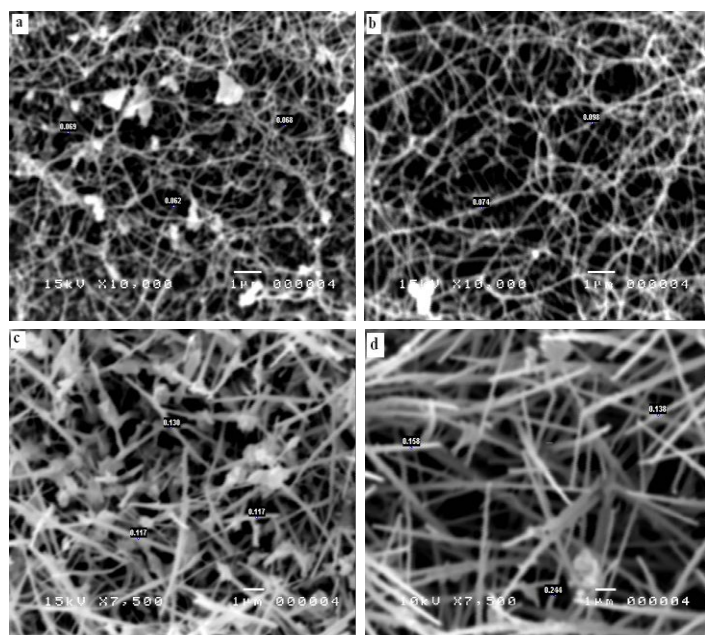
Approximately 35 mg of ZnO powder obtained from Sigma-Aldrich Singapore Pte Ltd is loaded into an ultrasonically-cleaned quartz tube with length of 220 mm, outer diameter of 11 mm and inner diameter of 8.5 mm. The quartz tube containing the source material is connected to a high-vacuum system via a flange equipped with a metal to glass quick-connect. The tube is then sealed using an appropriate mixture of liquefied petroleum gas and oxygen when the pressure is in the order of 10⁻⁶ torr. The sealed quartz tube is then set on a horizontal tube furnace which is programmed at a certain growth temperature and dwell time. The growth temperatures were set at 600°C, 800°C, 1000°C and 1200°C while the dwell time was adjusted from two hours to six hours in two-hour increments. A temperature gradient of about 300°C between the end of the quartz tube containing the source material and the growth site was maintained. This would cause the ZnO powder at the hotter end to evaporate and condense at the colder part of the quartz tube. At the end of the baking period, the furnace is allowed to cool down to room temperature naturally. The nanomaterials that are deposited on the walls of the quartz tube are subjected to SEM (JEOL 5310 series) and EDX analysis (Oxford with Link Isis) without further treatments. XRD (Bede Scientific D3 System) and PL (Olympus BX series) measurements were also done on the samples after the exact growth site of the nanomaterials was established using SEM.

3 RESULTS AND DISCUSSION

3.1 Growth temperature dependence

Figure 1 shows the SEM images of various nanostructures prepared at different growth temperatures with constant dwell time of two hours. Unreacted ZnO powder and web-like nanostructures at the initial stage of formation are observed at a growth temperature of 600°C. Randomly-oriented nanowires with typical dimension of less than 100 nm were grown at 800°C as evident in the SEM image. Needle-like structures with average diameter of 120 nm were synthesized at 1000°C. When the growth temperature is increased to 1200°C, blade-like structures with widths of approximately 200 nm are formed. It can be inferred from the SEM images that the dimensions of the synthesized nanostructures is dependent on the growth temperature.

At relatively lower temperatures the growth is preferred along a single direction such that one-dimensional nanostructures i.e., nanowires and nanowires are formed. With sufficiently higher energy of reaction, growth preference in this direction terminates and growth in other directions appears. This explains why nanostructures such as nanoblades and needle-like structures are observed at higher growth temperatures.



tures.

Figure 1: SEM images of ZnO nanostructures synthesized at different growth temperatures: (a) 600°C (b) 800°C (c) 1000°C (d) 1200°C

3.2 Dwell time dependence

Figure 2 compares the SEM images of ZnO nanostructures synthesized at a growth temperature of 1200°C but at different dwell times. The synthesized nanomaterials feature a width which ranges from 100 nm to 200 nm and length which extends from 5 microns to 10 microns. It can be noted that a longer growth time resulted in the formation of longer nanostructures. Moreover, an increase in the amount of the grown nanomaterials was observed as the growth time is extended. An increase in growth time corresponds to an increase in the

amount of ZnO vapor that migrate toward the colder region inside the tube and subsequently condensing on the walls resulting in the observed nanostructures. The one-dimensional nanostructures that were formed are approximately of the same size which suggests that dwell time does not contribute to the growth of ZnO nanostructures in other directions.

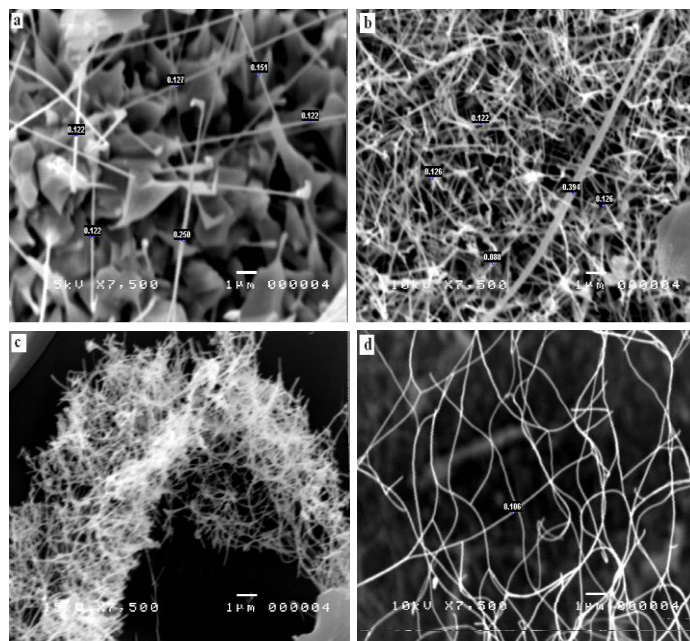


Figure 2: SEM images of ZnO nanostructures synthesized at different dwell times: (a) 2 hours (b) 4 hours (c) 6 hours (d) 8 hours

3.3 X-ray diffraction

XRD measurements were conducted to assess the crystal structure of the as-synthesized nanomaterials. Figure 3 presents the representative XRD spectra of the grown nanomaterials compared with other studies [18]. A prominent peak from the (101) plane can be observed while peaks from the (002), (101) and (103) planes were also detected. This polycrystalline nature of the samples can be verified from the SEM images. Determination of the lattice parameters was not successful owing to the relatively weak intensity of the XRD peaks of the nanostructures.

3.4 Photoluminescence

The representative room temperature PL spectra of the synthesized nanomaterials are shown in Figure 24-26. The spectra exhibited intense ultraviolet (UV) peak at approximately 380 nm and weak emissions in the visible light regime. It has been shown in previous studies that the UV peak can be attributed to the recombination of free excitons through an exciton-exciton collision process [19]. The band gap energy E_g can be computed from $E_g = hc/\lambda$ and is equal to 3.26 eV, close to the band gap of ZnO. Meanwhile, the deep level emissions are caused by singly ionized oxygen vacancy in ZnO and the emission results from the radiative recombination of photogenerated hole with an electron occupying the oxygen vacancy [20].

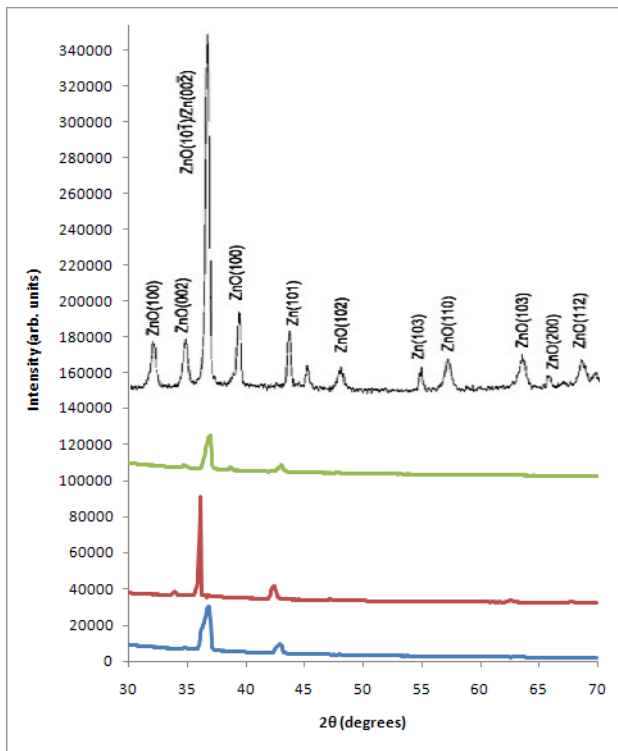


Figure 3: (a-c) Representative XRD spectra of the synthesized ZnO nanomaterials (d) XRD spectra of ZnO nanomaterials synthesized through thermal oxidation [18]

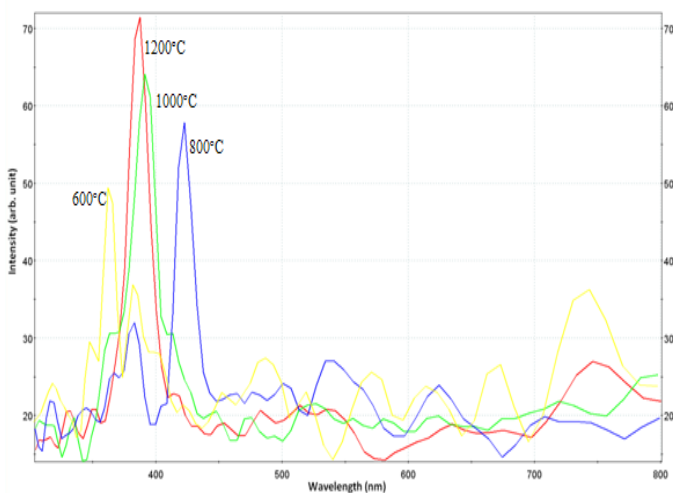


Figure 4: Representative PL spectra of ZnO nanomaterials

3.4 Proposed Growth Mechanism

The possible growth mechanism for the synthesis of ZnO nanostructures is through the vapor-solid process (VS) because no metal catalyst was used in this study [5]. It is proposed that the synthesis process is divided into two stages; nucleation and growth. As the source material is heated, it dissociates into ZnO in the vapor phase and transfers into the colder sec-

tion of the tube guided by temperature gradient that exists along the length of the tube. The rough inner wall of the quartz tube, providing an energy barrier in the vapor transport is believed to be the site of condensation and subsequent nucleation of ZnO molecules. The growth process proceeds as more ZnO molecules pile up at the nucleus eventually forming the nanostructure. Due to the preferred growth orientation of ZnO in the c-axis, one-dimensional nanostructures are synthesized. Meanwhile, with sufficient amount of energy, growth in other directions also appears, thus nanostructures like nanobelts, nanoblades and nanorods are also formed. The absence of a patterned substrate led to the formation of nano-materials that do not have a single orientation.

4 CONCLUSION

Zinc oxide (ZnO) nanomaterials were successfully synthesized through the horizontal vapor phase growth method. The results suggest that growth temperature and dwell time affect the structure of the ZnO nanomaterials. Various nanostructures which include nanowires, nanoblades and needle-like nanostructures were formed when the growth conditions were adjusted. It was shown from the PL measurements that the synthesized nanomaterials have excellent optical property. The nanomaterials, therefore, offer a wide range of applications in nanoscale optoelectronic devices.

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