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Controlling ZnO Nanostructure Morphology on Seedless Substrate by Tuning Process Parameters and Additives

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Abstract
In this, article ZnO nanostructure synthesized on seedless Si substrate by hydrothermal process using nutrient solution. Low concentration, 5 and 10 mM, equi-molar nutrient solution composed of zinc nitrate and hexamethylenetetramine (HMTA) and high concentration of 25 mM zinc nitrate and 12.5 mM hexamethylenetetramine (HMTA) with and without NH4.OH additions were used to synthesis ZnO nanostructure. The effect of precursor's concentration, growth temperature, and time were studied. The effects of these parameters on morphology and structure were investigated via SEM and XRD. It was found that the morphology reflect the dominate growth direction that could be tuning by controlling above parameters. High-density forest nanostructure achieved from high concentration nutrient solution with NH_4OH addition.
Keywords: hydrothermal, ZnO nanostructure, morphology, additive, and growth direction.

1. Introduction

Nanomaterials have attracted much attention due to their high performance in electronics, optics, and photonics. Typically, Nanomaterials are classified into three groups: 0-dimensional, 1-dimensional, and 2-dimensional.0-dimensional nanostructures, referred to as quantum dots or nanoparticles with an aspect ratio near unity (Liu at al. 2010 and Hoshino et al. 2004). 2-dimensional nanomaterials, as thin films that widely used as optical coatings, corrosion protection, and semiconductor thin film devices. One-dimensional (1D) nanostructures such as nanowires, nanorods, nanofibres, nanobelts, and nanotubes semiconductors have been of intense interest in both academic research and industrial applications.

One-dimensional (1D) zinc oxide (ZnO) nanowire is one of the most important nanomaterials for nanotechnology in today's research (Wang et al. 2009).It is a semiconductor material with direct wide band gap energy (3.37 eV) and a large excitation binding energy (60meV) at room temperature (Cai et al. 2008). It is also biocompatible, biodegradable, and biosafety for medical and environmental applications (Klingshirn et al. 2007). ZnO crystallizes in two main forms, hexagonal wurtzite and cubic zinc blended. Due to their remarkable performance in electronics, optics, and photonics, ZnO nanowires are attractive candidates for many applications such as UV lasers (Chu et al. 2011), light-emitting diodes (Na et al. 2009), solar cells (Sudhagar et al. 2011, nano-generators) (Wang et al. 2010), gas sensors (Xu et al. 2008), photo detectors (Lu et al. 2006), and photo catalysts (Cho et al. 2009). Among these applications, ZnO nanowires are being used increasingly as photo catalysts to inactivate bacteria and viruses and for the degradation of environmental pollutants such as dyes, pesticides, and volatile organic compounds under appropriate light irradiation (Sapkota et al. 2011 and Liu at al. 2010]

There are many available methods to fabricate one-dimensional ZnO nanostructures. .Among all of them, the most attractive synthesis technique for obtaining well-aligned ZnO nanowires, hierarchical or branched nanowires is the hydrothermal method. Compared with other high temperature physical or chemical vapor deposition methods, the low-temperature hydrothermal method offers the potential for much lower cost since no need for high-temperature manufacturing and vacuum processing. A lot of effort has been made to investigate the effect of synthesis parameters on the density, dimensions and quality of ZnO nanowires [10- 15]. Many focused on seeding layer effect (16-20), chemical reagent and their concentration effect on ZnO nanowire density (Wang et al. 2008 and Kim et al. 2011) morphology (Xu et al. 2008 and Kim et al. 2011), growth time and temperature (Baruah et al. 2009 and Yuan et al. 2011).We think there are still need to study the effect of additives, under different fabrication parameters, on ZnO nanostructure morphology.

Recently, it was founded that the introduction of ammonium hydroxide into the growth solution as an additive could efficiently affect ZnO nanowire morphology and their aspect ratio (Liu et al. 2007 and Hua et al. 2008).

In this Article, we study the synthesis of ZnO nanowires from zinc salts aqueous solution on seedless P type Si wafer with different concentration and growth time by hydrothermal method. ZnO nucleation and growth depends on the hydrolysis of zinc nitrate $[Zn(NO_3)_2.6H_2O]$ in water with the addition of hexamethylenetetramine(HMTA). Ammonium hydroxide was added to the growth solution to manipulate pH value and demonstrate its effect on morphology and structure. Role of nano gold as seedless layer on ZnO nucleation has been demonstrated also. The qualities of the resulting nanostructures have been characterized by scanning electron microscopy (SEM), and XRD. It was found that nanostructures morphology depends on precursor's concentrations, growth time, and temperature. NH_4OH addition affects greatly nanostructure growth

surfaces, directions, and morphology.

2. Experimental

In this work, p-type Si (100) wafer used as substrate for synthesis ZnO nanostructure on, to study the effects of various experimental parameters on its growth and morphology. Si (100) wafer substrate was cleaned by a standard cleaning progress. Firstly, ultrasonicated consecutively in acetone, ethanol, IPA (isopropyl alcohol), and de-ionized water each for 10 min; then it was blown dry with nitrogen gas and baked in oven at 200 °C for 10 min to eliminate adsorbed moisture. 20 nm Ti thin film was deposited before 50-nm-thick layer of Au on top of the Si wafer by ion beam evaporation. Ti was used as an adhesion layer to buffer the large lattice mismatch between Si (100) surface with native oxide and Au (111) surface and to improve the interface bonding. Au was expected to act as an "intermediate-layers" to assist the growth. Then the substrate was annealed at 300 °C for 30 min at argon environment. The next step was to prepare the nutrient solutions. Low concentration, 5 and 10 mM, nutrient solution composed of 1:1 ratio of zinc nitrate and hexamethylenetetramine (HMTA) and high concentration, 25 mM zinc nitrate and 12.5 mM hexamethylenetetramine (HMTA) with and without NH_4OH additions were prepared to study the effect of precursors concentration, growth temperature and time. All the chemicals were reagent grade from Sigma-Aldrich. The substrates were put face down at the top of the nutrient solution surface. Because of surface tension, the substrate could float at the top of the solution surface. Growth of ZnO NWs was conducted in a convection oven. The fabricated nanostructure were examined by scanning electron microscope (SEM) and XRD.

3. Results and Discussion

Generally in ZnO nanowire fabricated by hydrothermal process, when hexamethylene-tetramine ($(CH_2)_6N_4$, or HMTA) and $Zn(NO_3)_2$are used as precursors in the growth solution , the chemical reactions can be summarized in the following equations (Ladanov et al. 2011).

Decomposition reaction

$$(CH_2)_6N_4 + 6H_2O \longleftrightarrow 6HCHO + 4NH_3 \quad (1)$$

Hydroxyl supply reaction:

$$NH_3 + H_2O \longleftrightarrow NH_4OH \longleftrightarrow NH_4^+ + OH^- \quad (2)$$

Super-saturation reaction:

$$2OH^- + Zn_2^+ \longleftrightarrow Zn(OH)_2 \quad (3)$$

ZnO nanowire growth (dehydration) reaction:

$$Zn(OH)_2 \longleftrightarrow ZnO + H_2O \quad (4)$$

HMTA acts as a weak base and pH buffer it readily hydrolyzes in water equation (1).During solution preparation, Zinc nitrate dissolve completely in water, HTMA addition to the heated solution makes the solution milky like. This can be referred to ZnO dehydration from Zn hydroxyl as illustrated in above equations, which depends greatly on super-saturation reaction taken place before it. Therefore, if a lot of OH^- is produced in the solution, Zn^{2+} ions will precipitate out quickly at high pH environment. Result in, fast consumption of the nutrient with elimination of Zn^{2+} contribution in ZnO nanowire nucleation and growth (Xu et al. 2008 and Ashfold et al. 2007). It was found that one of the key parameters for ZnO nanowires nucleation is controlling the super-saturation reaction and reactants stability that depends on pH, precursor concentration, and solution temperature. It can be said, the morphology of the nanowires can be controlled by adjusting the reaction parameters, as precursor concentration, pH, and growth time and temperature.

To explore the influence of the growth time, temperature, precursor's concentration, and pH value on ZnO nanostructure density and morphology, a first series of experiments were performed with varying precursor concentration at fixed 1:1 ratio of zinc nitrate/HMTA.

For samples fabricated at low precursor equimolar solution (5 mM) and low temperature growth (65^0C), small aspect ratio, low densities and hexagonal shape ZnO nanorods were achieved, figure 1A, elevating growth temperature to 85^0C increase nanorods density but affect their shape to become prism like and branched with growth advancement as shown in figure 1B. Temperature plays an important role in ZnO nucleation, growth, and maintaining ZnO nanowires hexagonal shape. Many reasons can be considered to explain the effect of temperature on increasing ZnO nanostructure nucleation and growth. As we can see from equation (1), seven moles of reactants produce ten moles of products, increasing the reaction temperature lead to increase HMTA hydrolysis and push the equilibrium forwards associated with increase in entropy (Sheng et al. 2010 and Govender et al. 2004). The driving force for wet chemical process is the minimization of the entire reaction system free energy by product nucleation. It can be recognized that increasing temperature provide Zn ions with mobile energy and enhance ZnO nucleation to minimize their free energy. Change nanorods shape from hexagonal to prism like shape was probably due to the electrostatic interaction between the ions solution and ZnO polar surfaces, and as a result, higher Miller index surfaces became preferred.

Unless NH_4OH weak base and slightly tuned pH value when added to 5 mM nutrient solution at 85˚C but it has

great effect on nanorods shape and changes it to non-aligned hexagonal shape branched after 4 hours growth time as shown in figure 1C. ZnO grows on<111> oriented nano gold layer has Wurtzite structure along high-energy polar surfaces due to the small lattice mismatch between them (Sheng et al. 2010, Laudise et al. 1960 and Zhenqing et al. 2012). From XRD spectrums, figure 2, (002) is the favorite growth surface for ZnO nanorods fabricated at solution without any addition, figure 2a. While dominate growth surface with NH_4OH addition and after 4 hours growth become (112), figure 2b, that synchronize with nanorod branching. This give evidence that the nanorods branched, referees to the growth direction changes with depletion of Zn ions at solutions contain ammonia.

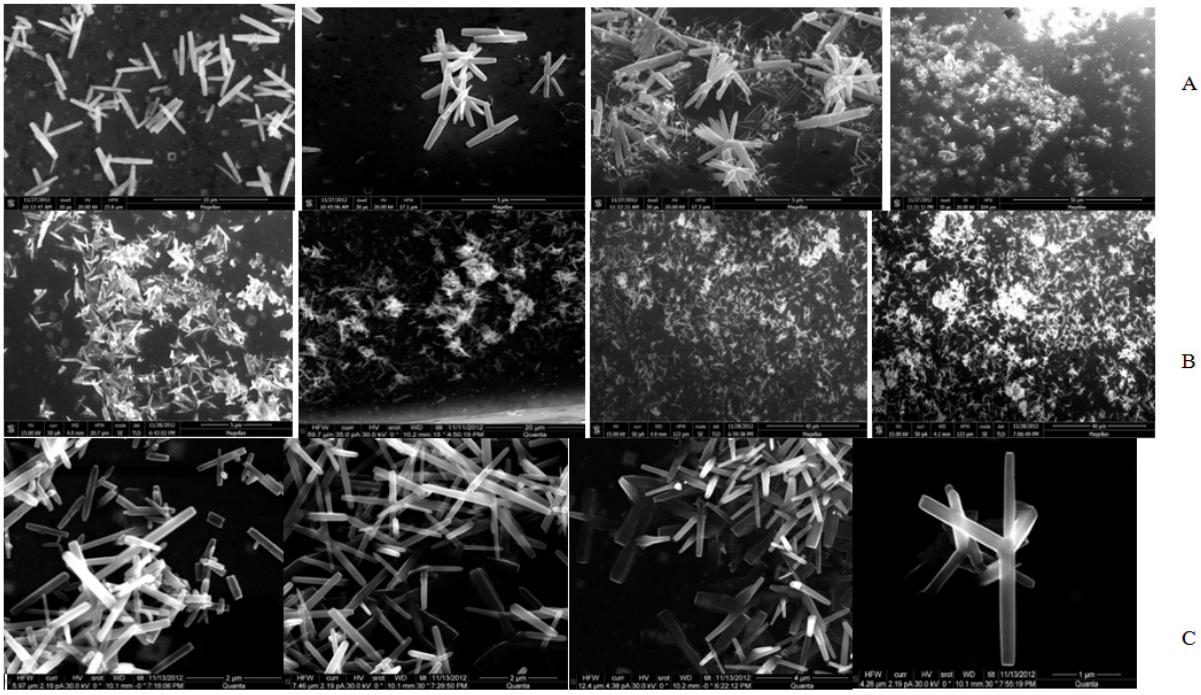
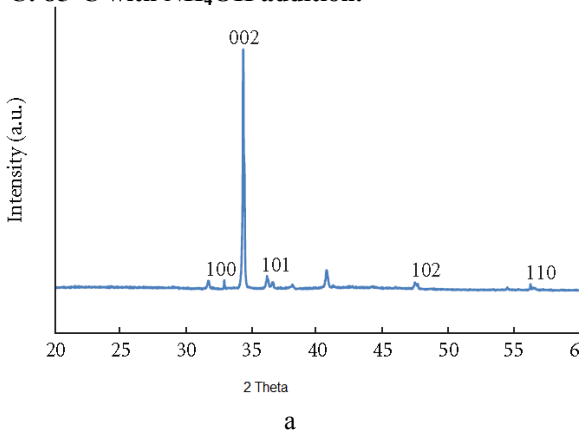
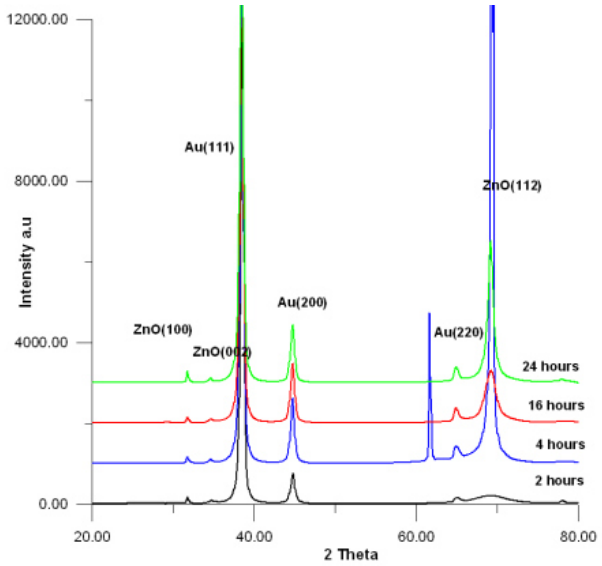


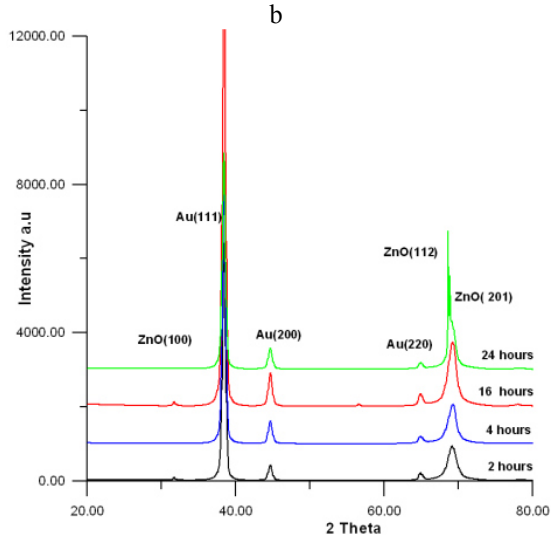
Figure 1- SEM images for ZnO nanorods fabricated at equimolar 5 mM solution different growth time with and without NH4.OH addition. growth time, a: 2 h, b: 4 h, c: 16 h, d: 24 h. growth temperature and additives A: 65^{0}C B: 85^{0}C C: 85^{0}C with NH_4OH addition.



a



b



C

Figure 2- XRD spectrums for ZnO nano structures fabricated at equimolar solution, a: without any addition b: 5 mM with NH_4OH addition c: 10 mM with NH_4OH addition.

Increased precursors concentration provides a lot of ZnO nucleates and densify nanorods. It was reported that solution environment that consist sufficient OH^- encourage nucleation and growth, while H^+ inhabited it (Sheng et al. 2010). With fixed precursor's ratio 1:1, 10 mM solution 85^0C solution temperature the prism like-shape nanorods are branched early, with ions depletion lateral growth direction increased until getting continues film as shown in figure 3A. As explained before NH_4OH addition to the solution slightly tuned pH value and effect greatly nanorods density and growth rate as shown in figure 3B&C. Also Its addition change the dominate growth surface to (112) from the first growth hours as shown in XRD spectrum, figure 2c, this replicated on their shape that become typical hexagonal dumbbell-like.

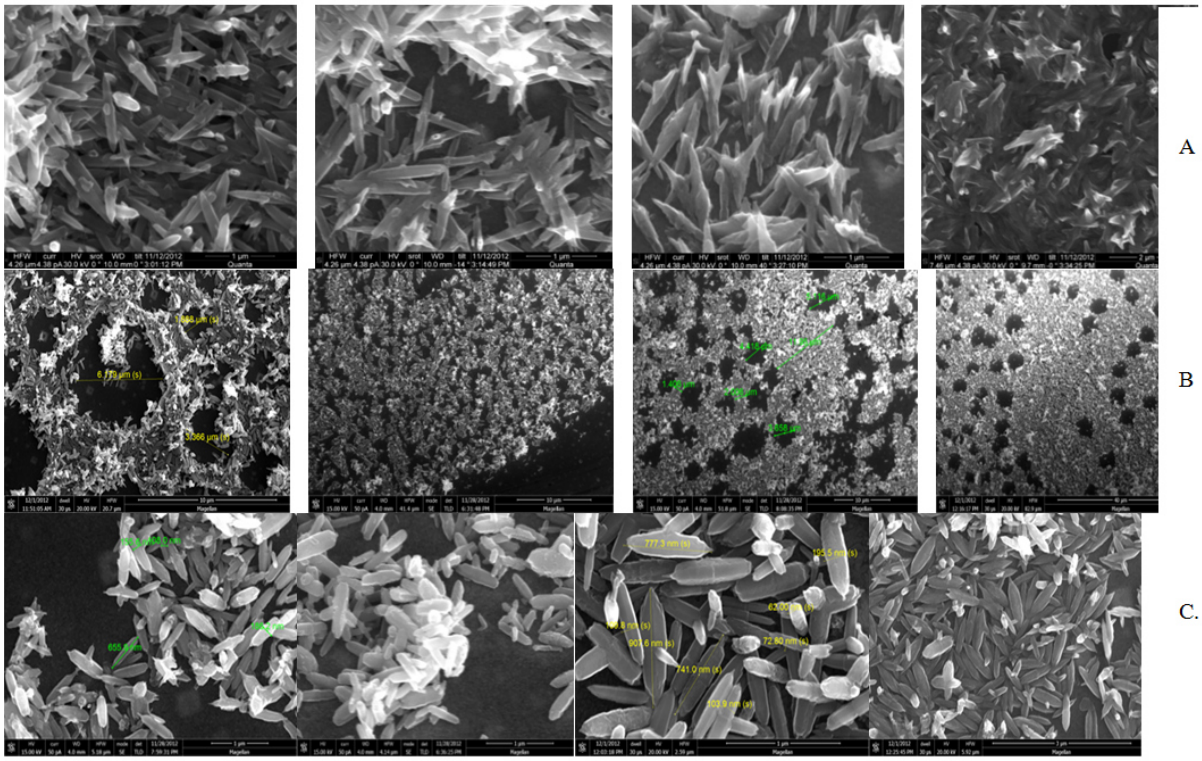
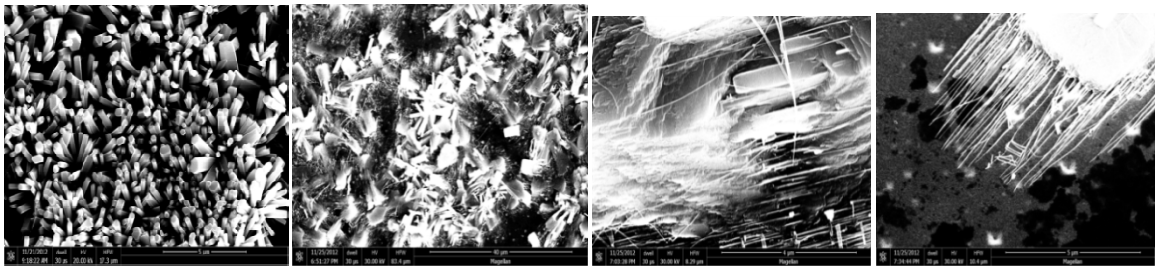


Figure 3- SEM images for ZnO nanorods morphology fabricated at equimolar 10 mM solution with and without NH_4OH addition. Growth time, a: 2 h, b: 4 h, c: 16 h, d: 24 h. A: without addition, B: with NH_4.OH addition, C: High magnification With NH_4OH addition.

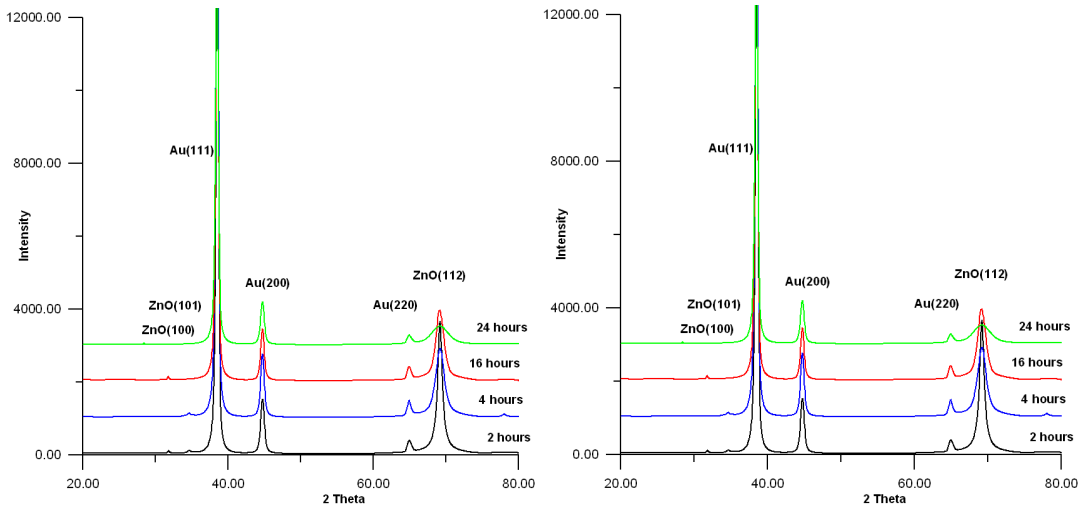
Pervious researches tended to refresh growth solution every 4 hours by addition of new precursors to the growth solution, they found that ZnO nucleus are easily destroyed by fresh growth solution, due to low chemical stability and high mobility (Postels et al. 2007 and Tianet al. 2011). In this work, without refreshing solution, we found our nanorods grow with time. It was reported before; NH_4OH could stabilize Zn^{2+} through reversible reaction of consuming and decomposing of zinc–ammonia complex, maintaining a stable level of Zn^{2+} in the solution. At growth temperature (typically 70– 95 °C), heterogeneous growth on the substrate promoted while the homogeneous nucleation in the bulk solution suppressed so the growth could last for a long time without replenishing the solution (Sheng et al. 2010). Under this environment, stable level of Zn^{2+} in the solution, an expectation of local rise in pH value may assist initiation of secondary nucleate branches on nanorods side surface with advanced growth (Zhang et al. 2006), this may explain the change in ZnO nanorode dominate growth surface and branching with NH_4OH addition to the growth solution.

To avoid Zn ions depletion from the fabrication solution and demonstrate effect of NH_4OH addition on ZnO nanorod morphology and density, another experimental series with nutrient to HMTA ratio 2:1 (25 mM nutrient, 12.5 mM and 0.35 mM NH_4OH) were carried out. At the first growth hour's high density and vertically aligned ZnO nanorods achieved from unclear high concentration solution, figure 4a. With advanced growth vertically aligned nanowires nucleate and growth together with nanorods to form big bundle nanorods, figure 4b, that dissolved after long time exposure to aqueous solution as shown clearly in figure 4 c&d. Unclear high concentration aqueous solution has high Zn^{+} concentration that precipitate directly after solution preparation. Precipitation and Zn ions depletions continue with time leading to pH value increased that lead to dissolve ZnO in resultant alkali solution, solubility increased with alkali concentration and temperature (Demianets et al. 2002). The unclear nutrient solution XRD spectrum revile the domination of (112) surface from the early growth stages as shown in figure 5a.



a b c d

Figure 4- SEM images for ZnO nanorods morphology fabricated at unclear 25 mM nutrient, 12.5 mM, and 0.35 mM NH_4OH. Growth time, a: 2 h, b: 24 h, c and d: ZnO nanorods images at high magnification.



a b

Figure 5- XRD spectrums for ZnO nano structures fabricated at 25 mM nitrate : 12.5 HMTA with NH_4OH addition a: unclear solution b: clear solution.

ZnO nanowires fabricated at cleared 25 mM nutrient, 12.5 mM, and 0.35 mM NH_4OH solution, pH 5.43, formed high-density forest like nanostructure. From the first hours, nanowires nucleate at high rate on seedless substrate, nano gold particle boundaries, as shown in high magnification SEM images they are branched many times quickly. Forest like nanostructure achieved after 2 hours as shown in figure 6A. Fixed pH value for long time indicates stable precursor's concentration solution. Stable high precursor's concentration solution with moderate pH environment decrease HTMA hydrolyses (Govender et al. 2004), which lead to increase pH value locally and assist initiation of secondary nucleate branches on nanowires side surface with advanced growth.

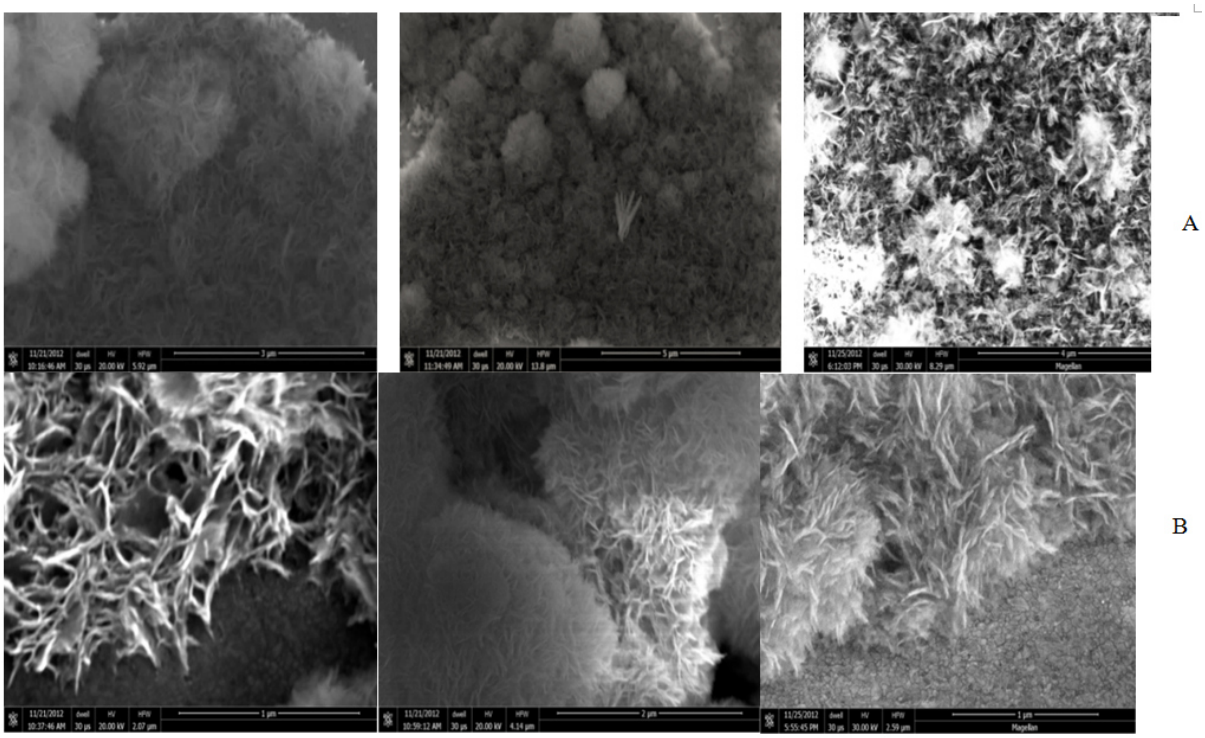


Figure 6- SEM images for ZnO nanorods morphology fabricated at clear 25 mM nutrient, 12.5 mM HMTA, and 0.35 mM NH_4OH. Growth time, a: 2 h, b: 16 h, c: 24 h.
A: moderate magnification B: high magnification

For clear nutrient solution and at their first growth hours the favored growth surface is (112) after short time, then (100) together with (112) become the favorite's growth surfaces as shown in figure 5a. That replicated in nanowires branching many times to form forest like nanostructure from the first growth hours.

4. Conclusion

The morphology of ZnO nanorods could be tuned and was found to be controlled by the concentration of the reactants, HMTA and $Zn(NO_3)_2$ and growth solution temperature. ZnO nanorods density, fabricated on Au seedless substrate, increased with $[Zn^{2+}]$ at low concentrations (5 and 10 mMnutrient solution) and decreased with $[Zn^{2+}]$ at high concentration levels (25 mM nitrate) for cleared and unclear solution. For low concentrations nutrient solution, nanorodes morphology was very sensitive to the growth temperature. When growth temperature increased to 85°C, the nanrodes shape change to prism like and branched with growth advancing. $NH_4.OH$ addition affects greatly ZnO nanostructure morphology; it could tune their shapes from prism like to hexagonal and increase their densities. At high concentration, levels (25 mM nitrate) with $NH_4.OH$ addition nanostructured are sensitive to pH value and Zn^{+2}concentration. Clear solution obtained after preparation has fixed pH value for long time and stable precursor's concentration solution, so high density branched nanowires, with high aspect ratio were achieved. While unclear solution is unstable precursor's concentration, its pH value changed with time, lead to non-uniform growth.

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