Electrochemical self-assembly of bunch-shaped ZnO nanowire without catalysts

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Abstract:
There are many types of metal oxide nanostructure and one of them is zinc oxide (ZnO). Despite of vast field of application for this material, the fabrication process of nanostructure (ZnO) is rather costly or complicated due to exotic equipment or reagent required. To the leading of our understanding, there are no details about synthesizing the bunch-shaped ZnO nanowire patterns on silicon substrate. A series based on aqueous medium composition: (x) Zn(NO₃)₂ + 0.1 NaOH, where 0.005 ≤ x ≤ 0.2 mol% is prepared using chemical bath method. The distribution and size of ZnO nanostructure was determined using FESEM spectroscopy. Meanwhile, EDX spectra show the presence of ZnO nanostructures in all samples. These researches generate new knowledge on embodiment of ZnO nanostructures on silicon thin film which may useful for finding material with high optical quality for diverse application in photonic devices.

Keywords: ZnO, nanostructured, thin film

1. Introduction
In the past few decades, there have been more studied in structural and optical behaviour of the ZnO nanostructures due to their technology and commercial applications. Thin film deposited with ZnO nanostructures presented unbelievable chances in photonic substances domain since of their vary of implementations by broaden from light energy conversion to detection, random laser, gas sensor, light emitting diode and solar cell technology [1-3]. Despite of that, the characterize of ZnO vigorously rely on its morphology and microstructure in those applications [4]. Hence, the investigation towards control the shape, size and microstructure of ZnO become crucial [5]. The deposited of ZnO material on substrates even though remain as a challenging issue due to the basic physics behind the properties of material deposition still are lacking.

Recently, there are many techniques available have been used to deposited the ZnO materials on the thin film substrates. In general, the depositions of material on the substrates are categorized in physical or chemical. However, the chemical bath deposition technique have attracts extensively attention
of many researcher owing to its feature of the sort as low temperature, low cost, simple and easily coating of the substrate surface compare to the physical technique which using more sophisticated equipment [6-7]. Despite much research the mechanism of growth of ZnO nanostructure using chemical bath deposition is far away from being realize. Orderly sample emulsion with optimized the solution concentrations, controlled growth of nanostructures and particular characterization are required.

Synthesis and characterization of thin film deposited with nanostructure have been studied widely through optical, structural and morphology. ZnO materials become one of a good candidate due to their characteristic like outstanding chemical firmness, non-poisonous, good electrical, visual and electrifying property. However, the utilization of ZnO nanostructure materials applications which generally needs the crystalline morphology, direction and surface of nanostructures development need to be well controlled in order as optoelectronic material used in photonic and electronic application. To overcome this limitation, the use of optimization the solution concentration for aqueous medium in chemical bath deposition has been found a successful way to control the growing of ZnO nanoparticles stick on thin film substrate. Systematic experimental study will be made to analyze the structural and morphology of ZnO nanostructure. To recognize and ascertain the procedure of ZnO nanoparticles we will prepare a series of silicon substrate deposited using zinc nitrate and sodium hydroxide as aqueous medium in chemical bath deposition and characterize them.

In this study, the investigation will be carried by deposited ZnO nanostructures on silicon thin film. The morphology of ZnO nanostructures in substrates will be investigated to complete the samples with optimum utilization aqueous medium compositions applying chemical bath techniques. The interpretation on the process of ZnO nanostructures restoring the morphology and structural characteristics can be applied in the growth of photonic technology. This work will create the knowledge to enhance the morphology and structural properties of ZnO nanostructures deposited for wide application possibilities. Alert sample composition, controlled of aqueous medium composition, ZnO nanostructures growth of desired sizes, shape and pattern is the difficult piece of work that will be talented. Evaluation of morphology and structural aspect are the principal aim to be attained.

2. METHODOLOGY

The sequence of sample was conformation using chemical bath technique. The substance for the sample preparation of ZnO nanostructures are practically in using silicon as substrate meanwhile zinc nitrate as precursor and sodium hydroxide for the aquas medium. The samples were prepared with dissimilar concentration of zinc nitrate due to find the optimization of solution concentration for ZnO nanostructures fabrication.

First, the silicon substrates where the deposition of ZnO will take place were prepared respectively. Then, the aqueous medium which used in this chemical bath deposition was prepared using the reagent zinc nitrate and dissolve in common chemical reactive salts, sodium hydroxide. Following, 60 ml mixture of zinc nitrate and sodium hydroxide were put in a beaker. The silicon substrates which prepared under typical conditions were standing suspended in the beaker, meanwhile water bath was used at constant temperature of 85 - 90 °C. Generally, water bath is used to obtain the homogeneous temperature for this experiment and the deposition time was 90 minutes. The silicon substrates with deposited films were removed, rinsed with distilled water and pull out of dry after 90 minutes of deposition. The as-deposited ZnO thin films were also heated up at 200 °C and 300 °C in a furnace for 20 minutes.

All of the samples was fabricated by subsequent the same procedure and keep in vacuumed desiccators to delete any contamination and moisture. The characterization of prepared sample will be using various spectroscopy techniques. Figure 1 depicts the experimental of sample preparation meanwhile Figure 2 show the schematic diagram for preparation of sample.
This experiment was used analytical reagents zinc nitrate and sodium dioxide as aqueous medium in the chemical bath. The compositions for aquas medium in order to fabricate the ZnO nanostructures in the sample are:

\[(x) \text{Zn(NO}_3\text{)}_2 + 0.1 \text{NaOH}\]
where $0.005 \leq x \leq 0.2$ mol%. The possible chemical reaction in the solution mixture in order to obtain the ZnO nanostructure is as follows:

\[
\begin{align*}
\text{NaOH} & \rightarrow \text{Na}^+ + \text{OH}^- \\
\text{Zn(NO}_3\text{)}_2 & \rightarrow \text{Zn}^{2+} + 2\text{NO}_3^- \\
\text{Zn}^{2+} + 2\text{OH}^- & \rightarrow \text{Zn (OH)}_2 \\
\text{Zn (OH)}_2 & \rightarrow \text{ZnO}
\end{align*}
\]

During the growth process, first ZnO nucleus growth takes place which then aggregates and produces ZnO nanoparticles by Ostwald ripening. Nanoparticles crystallize and aggregate with each other through Van der Waals forces and hydrogen bonding and give ZnO nanostructures. Figure 3 depicts the schematic diagram for chemical bath deposition technique.

![Figure 3. Schematic Diagram for Chemical Bath Deposition.](image)

Generally, the study of this research is started by preparation of silicon (Si) wafer. Then, the deposition of ZnO are used an appropriate amount of zinc nitrate (Zn (NO\(_3\))\(_2\)) (purity, 98.0%) and sodium hydroxide (NaOH) (99.0%). The series of sample was prepared and followed by the detail structural and morphology properties were investigated using several spectroscopic measurements.

The calculation to measure the analytical reagent for aqueous medium since the chemical bath deposition is a technique which control the homogenous precipitation of substance in the solution are used as equation 1:
\[ \rho = \frac{m}{V} \]  \hspace{1cm} (1)

Where, \( \rho \) is density of solution, \( m \) is mass of solution and \( V \), is volume of solution. The nominal composition of aqueous medium for this study is shown Table 1 meanwhile Table 2 represent the experimental configuration.

**Table 1.** The composition of zinc nitrate concentration.

| Sample | Concentration of Zn(NO₃)₂ | Volume of Aquas Medium | Volume of Zn(NO₃)₂ |
|--------|----------------------------|------------------------|-------------------|
| Sample 1 | 0.005 M | 60 ml | 0.3 ml |
| Sample 2 | 0.01 M | 60 ml | 0.6 ml |
| Sample 3 | 0.05 M | 60 ml | 3.0 ml |
| Sample 4 | 0.10 M | 60 ml | 6.0 ml |
| Sample 5 | 0.20 M | 60 ml | 12.0 ml |

**Table 2.** Experimental Configuration.

| Sample | Temperature (°C) | Duration (minutes) | Volume (ml) | Concentration |
|--------|------------------|--------------------|-------------|---------------|
| Sample 1 | 80-90 | 90 | 60 | 0.005 M Zn(NO₃)₂ + 0.1 M NaOH |
| Sample 2 | 80-90 | 90 | 60 | 0.01 M Zn(NO₃)₂ + 0.1 M NaOH |
| Sample 3 | 80-90 | 90 | 60 | 0.05 M Zn(NO₃)₂ + 0.1 M NaOH |
| Sample 4 | 80-90 | 90 | 60 | 0.10 M Zn(NO₃)₂ + 0.1 M NaOH |
| Sample 5 | 80-90 | 90 | 60 | 0.20 M Zn(NO₃)₂ + 0.1 M NaOH |
3. RESULTS AND DISCUSSIONS

According to Urgessa, the ration of concentration in aqueous medium can affected the shape, size and distribution of ZnO deposited on substrates. From the Figure 4, the bunch-shaped ZnO nanowire arrays were observed. More nanowires intended to aggregate to form bunch shape with addition of zinc nitrate at the same temperature and deposition time. The presence of bunch-shaped nanowires can be well explained by a great amount of Zn(OH)$_2$ precipitations in the aqueous solution. The formation of Zn(OH)$_2$ precipitations in the solution prohibited the forced hydrolysis of anhydrous zinc acetate and further growth of ZnO.

The micrograph also shows that the ZnO cover the substrate more uniformly and are aligned predominantly perpendicular to the substrate. The increasing of zinc nitrate change the orientation, shape and size of ZnO nanostructure can be shown from the sample 1 until to sample 5. Figure 4 illustrate the ZnO nanostructures obtained from different composition of zinc nitrate.

![Sample 1](image1)
![Sample 2](image2)
![Sample 3](image3)

![Sample 4](image4)
![Sample 5](image5)

*Figure 4. ZnO nanostructures obtained from different composition of zinc nitrate*

Energy dispersive spectra confirm the presence of ZnO nanostructure in all samples since elements zinc and oxygen was detected. During deposition process, the oxygen molecular will be encounter chemical bonding with aqueous medium for shaping the ZnO nanostructures. The oxygen percentage increase proportional to the increment of zinc nitrate due to the interaction of hydroxyl group with crystallization of ZnO nanostructures [8-10]. Figure 5 displays the EDX spectra of the all sample where the elements (carbon, silicon, oxygen and zinc) present in the silicon thin film.
Figure 5. EDX spectrums for all samples
4. CONCLUSION

Careful synthesis and thorough characterization of ZnO nanostructures was the focus task to achieve the objectives of this work. Firstly, the deposition was carefully prepared using chemical bath technique in order to control growth the crystallization ZnO. Incorporation of ZnO nanostructures was carried out to investigate the structural, morphology and optical properties. Consequently, the subsequent judgement is drawn establish on the analyzed data:

a. Series of silicon thin film deposited with ZnO based on aqueous medium composition: \((x)\ Zn(NO_3)_2 + 0.1\ NaOH\), where \(0.005 \leq x \leq 0.2\ \text{mol}\%\) successfully prepared. All series of sample was prepared using different concentration of zinc nitrate in order to study the influence of composition on samples.

b. The micrograph obtained from FESEM spectroscopy shown the crystallization of ZnO nanostructure change by the increment of zinc nitrate. Sample 5 shown the ZnO nanorods array.

c. The EDX spectra showed the traces of all the elements (carbon, silicon, zinc and oxygen), present in the sample. Interaction of hydroxyl group with crystallization of ZnO nanostructures increases the oxygen percentage in samples.

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