Effect of Deposition Time on Material Properties of ZnO Nanorods Grown on GZO Seed Layer by CBD

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ABSTRACT

ZnO nanorods (ZNRs) were grown on Ga-doped ZnO (GZO) through a two-step procedure, involving pre-treatment to form the seed layer followed by growth of the nanorods through chemical bath deposition (CBD) method. The study determines the effect of different growth deposition times (ranging between 30 and 150 min) at 90°C growth temperature and 0.05M concentration of precursor solution. The influence of this growth parameter on structural and optical properties of ZNRs thin films is presented. The pattern of X-ray diffraction displayed ZNRs thin films with a polycrystalline hexagonal structure. The estimated crystallite size increased with deposition time while the calculated strain was found to decrease with increase in time, an implication of improved crystallinity at longer deposition time as displayed by highest XRD peak intensity at 90 min. The scanning electron microscopy and atomic force microscopy images exhibited various types of morphologies at different deposition time with homogenously distributed nanorods observed at 90 min. An inverse relation between the optical band gaps and deposition growth time of the prepared nanorods was observed. The ZNRs sample grown on the transparent conductive film of GZO, with high luminescence and perfect crystallization produced at the 90 min growth deposition time could suitable for use as a photoanode component of the dye-sensitized solar cell.

Keywords: ZnO Nanorods, Thin Films, Crystal Structure, CBD, Spin Coating

Introduction

One-dimensional (1D) nanostructures such as nanotubes, nanoribbons, nanowires, nanorods, nanobelts, and nanobelts have taken centre stage in the past few years, this came after the carbon nanotubes was discovered [1-5]. The 1D nanostructures have inspired immense research in the field of science because they exhibit excellent optical, and electrical properties which are displayed in their vast applications in various nanodevices owing to their large surface area.

Many reports have described ZnO nanorods (ZNRs) preparation using one-step aqueous method such as pulsed laser deposition, chemical vapor deposition and electrochemical deposition [6-8]. Complicated procedures, high temperatures, and sophisticated equipment are reported to have been used in the mentioned methods of ZNRs synthesis. The chemical bath deposition (CBD) method, on the other hand, is quite a facile and inexpensive process which requires simple apparatus and most importantly, the nanorods can be grown at low temperatures [9, 10]. Additionally, the shape and size of the ZNRs can easily be controlled using the CBD technique by fine-tuning the growth parameters such as stoichiometric ratios of the reagents, solution concentration, growth temperature, growth time, and pH of the solution [11-13].

As far as the CBD technique is concerned, controlling the size and morphology of the nanorods has proven to be challenging that is why most researchers use a two-step process which involves pretreatment of the substrates and chemical bath deposition process [14, 15]. Study reports that the ZNRs grown on Si substrate through CBD method displayed poor results and difficulty in reproducibility [16]. It is, thus, commonly agreed that ZnO seeding, by spin coating or sputtering, is essential for easy and convenient growth of a well-aligned ZNRs perpendicular to the substrates [17, 18].

Ga-doped ZnO (GZO) is identified in this study, as transparent conducting oxide seed layer because, it does not easily undergo oxidation like aluminium and due to the fact that ionic and covalent radii of Ga and Zn are pretty close [19]. We believe, achieving control over the properties and characteristics of ZNRs through the seed layer doping has not been widely reported in literature. The report of this study will add to the body of knowledge on ways of improving the versatile properties of ZNRs deposited on the GZO transparent oxide seed layer. A promising combination to be employed for use as photoanode in dye-sensitized solar cells application. Indeed, ZNRs show distinct morphologies in different deposition growth times with well-aligned rods obtained at 90 min.
Experimental Procedure

The reagents used are zinc nitrate hexahydrate (Zn (NO₃)₂, 99.9% purity), sodium hydroxide (NaOH), gallium nitrate hexahydrate (Ga(NO₃)₃, 99.9% purity), HMTA (C₆H₁₂N₄, 99.9% purity) and distilled water. The reagents are all of analytical grade so no further refinement was not required. ZnO nanorods were grown on the GZO seed layer through a two-step CBD method.

Firstly, as prepared and optimized GZO nanoparticles were spin-coated on glass substrate to make a seed layer. The GZO nanopowders were prepared as described [20]. The GZO powder was ground, dissolved in suitable solvent and mixed into a homogenous paste to form the spin coating solution. SPEN 150 spin coater operating at 2000 rpm for 30s was used to spin-coat the solution on the glass substrate and the film so formed pre-annealed on a hot plate for 10min at 250 °C. The GZO thin film deposition and pre-heating procedures were done repeatedly 10 times to obtain suitable thickness and uniform coverage of the seed layer and eventually post annealed using a furnace in air from room temperature (RT) to 300 °C for 120 min duration. Secondly, the GZO seeded-substrate was immersed in reaction bath of precursor solutions to achieve growth of the ZNRs. The reaction bath was formed by dissolving 0.05 equimolar solutions of Zn (NO₃)₂, 9H₂O and HMTA in distilled water in a 100 ml beaker at RT. To this, the reaction vessel containing the reaction bath and the seeded glass substrate was placed in a thermostatically controlled water bath. To monitor the growth process in CBD set up, the deposition growth time was varied from 30-150 min. Finally, the glass substrate film was removed from the reaction vessel, and rinsing was done using running water and thereafter left to dry in an oven at 70°C for about 5 min.

Various measurements were conducted on the as grown ZNRs. The crystal structures were examined by X-ray diffraction (XRD) sing a Bruker D8-Advance X-ray diffractometer (with monochromatic CuKα radiation, λ=1.5406 Å). Scanning electron microscope (SEM, JEOl JSM-7800F) was used to characterize the morphology, and accompanying Oxford Aztec EDS (Energy-dispersive X-ray spectroscopy) measured the elemental composition of the products. An atomic force microscope (AFM, Shimadzu SPM – 9600) was used to study surface topography. The optical emission spectra were measured on a UV–Vis-IR spectroscopy (Perkin Elmer Lambda 950). While the photoluminescence (PL) spectroscopy studies were conducted by means of a Cary Eclipse fluorescence spectrophotometer; model LS-55.

Results and Discussion

XRD Analysis

Figure 1(a) displays the XRD patterns of the ZnO NRs thin films grown on GZO seeded glass substrate for varied deposition times (30-150 min). All patterns reveal the distinct diffraction peaks which are characteristic of the hexagonal crystal structure well indexed to the JCPDS card No. 75-1526, a = 3.220 nm, and c = 5.200 nm of ZnO, corresponding to the [100], [002], [101], [102], [110], [103] and [112] planes. The XRD spectra of ZNRs show general enhancement of peak intensities indicative of an improvement in crystallinity. The diffraction peak intensity increased to a maximum at 90 min and decreased for longer deposition time. No other characteristic peaks from the XRD pattern could be identified which confirms high level crystalization of the samples and existence of only single phase of hexagonal ZnO wurtzite structure.

Clearly, as could be seen in Figure 1(a), the intensity of [002] plane is the most enhanced as compared to the usual [101] most intense reflection in the standard pattern of ZnO. This observed phenomenon indicates a preferred growth of ZNRs along the c-axis [21]. More often, to characterize the orientation of ZNRs, intensity ratios of (002) and (101) planes is used because it is [002] plane only which can give any further information and evidence on the preferred c-axis orientation of ZNRs. Thus, the degree of c-orientation described by the relative texture coefficient (TC) was calculated using the expression [22].

The calculated values of TC for (002) and (101) diffraction peaks denoted as TC(002) and TC(101), respectively for different deposition times are presented in Figure 1(b).

Figure 1(b): The Texture Coefficients of [002] and [101] Planes of ZNRs Arrays as a Function of Growth Time. Figure 1(b) shows that the TC values of (002) planes are greater than that of (101) planes confirming the preferential growth of the ZNRs in the c-axis as mentioned earlier. The growth along this direction is favored because any growth deviating from c-axis get obstructed due to high density of the nanostructures [23]. The NRs, therefore, are pertinent to grow along the c-axis when competition and optimization of rules are put into consideration. Studies have shown that the [101] surface face grows the fastest in nanopowders, as the growth progresses. However, the [002] plane in NRs thin films grows faster and increase in orientation at the expense of the [101] plane due to higher rates of deposition and growth along the c-axis resulting in reduced growth along the [101] orientation [24]. It is also vital to note that the TC values of (002) plane increases as the deposition time increase. Similarly, the TC values of (101) plane increased, albeit, up to 90 min of deposition time and declined thereafter.
The full width at half maximum (FWHM) of the as-prepared ZNRs thin films was obtained from all the diffraction peaks. It was found that FWHM values decreased with increase in deposition time as displayed in Figure 1(c). These FWHM values were then used in calculation of crystallite sizes of characterized samples using Debye Scherrer formula [25]. The sizes of the crystallites were found to increase as the deposition time increase (30 - 150 min) as shown in Figure 1(c). The estimated crystallite sizes were 21.31, 22.62, 23.81, 21.81 and 31.04 nm for 30, 60, 90, 120 and 150 min of deposition time respectively.

With an increase in deposition time, peaks shift to lower 2θ angle was observed in the diffraction planes of ZNRs (Figure 1(d)). This shift to lower diffraction angle, attributed to lattice expansion, is a further confirmation of an increase in the crystallite size with increase in deposition time. The verification of expansion of lattice parameters of ZNRs was done by calculating the values of dominant diffracted peaks of the XRD spectra and tabulated in table 1 [26]. To compare the value of bulk ZnO (c = 5.204 Å), the calculated values are slightly lower demonstrating that the characterized samples may be under some strain.

\[ \varepsilon = \frac{\beta}{4 \tan \theta} \]  

(1)

Where, \( \theta \) is the angle of diffraction and \( \beta \) is the FWHM.

Similarly, calculation of the lengths of the dislocation density (\( \delta \)) was established using equation (2) [28];

\[ \delta = \frac{1}{D^2} \]  

(2)

Where D is the crystal size obtained from the XRD pattern.

Table 1: A table displaying the lattice constant, the AFM RMS values and particle sizes, crystallite size, [002] plane peak position, strain and dislocation density of ZNRs at the different cell at varied deposition growth time.

<table>
<thead>
<tr>
<th>Growth time (min)</th>
<th>Lat. Constants (Å)</th>
<th>AFM analysis</th>
<th>Crystallite size (nm)</th>
<th>[002] Plane Peak Position (°)</th>
<th>Strain (e)</th>
<th>Dislocation density (°/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>3.2140</td>
<td>5.19819</td>
<td>1.6174</td>
<td>33.3</td>
<td>21.31</td>
<td>34.8</td>
</tr>
<tr>
<td>60</td>
<td>3.2141</td>
<td>5.20129</td>
<td>1.6181</td>
<td>-</td>
<td>22.62</td>
<td>34.8</td>
</tr>
<tr>
<td>90</td>
<td>3.2144</td>
<td>5.20215</td>
<td>1.6184</td>
<td>39.6</td>
<td>23.81</td>
<td>34.79</td>
</tr>
<tr>
<td>120</td>
<td>3.2140</td>
<td>5.19915</td>
<td>1.6081</td>
<td>-</td>
<td>21.81</td>
<td>34.8</td>
</tr>
<tr>
<td>150</td>
<td>3.2149</td>
<td>5.20115</td>
<td>1.6178</td>
<td>95.0</td>
<td>31.04</td>
<td>34.78</td>
</tr>
</tbody>
</table>

It could be deduced from Table 1, that both the values of the strain and the dislocation density were inversely related to the deposition growth time. The dislocation density gives an indication of the dislocation network in the structure of the particle, therefore the decrease with increase in the deposition growth time indicate improved crystallinity.

**SEM Observations**

The SEM micrograph images of ZNRs at different deposition times are presented in Figure 2. As shown, remarkable morphological transformations and improvements have been observed on the as-prepared ZNRs thin films as the time increases. For the shorter duration of deposition, tiny and agglomerated mixtures of nanorods and nanospheres could be seen which changed into well-aligned and uniformly distributed ZNRs at 90 min. The film deposited at longer deposition time, however, showed an enlarged morphology of flower-like structures of ZNRs.

Figure 2: SEM Images of ZNRs Prepared at Deposition Times (a) 30, (b) 90 and (c) 150 min
Apparently, at shorter deposition time nucleation takes place where
the growth mechanism processes (diffusion and aggregation) occur
as explained [29]. Furthermore, the differences in morphology,
density, orientation and alignment of ZNRs can be further
explained in view of the formation mechanism that governs CBD
method where solid phase is formed on a substrate from an aqueous
solution through nucleation and growth processes [30]. As the
growth time progressed, the dimensions of the nanorods increased
but stopped after some period of time and erosion process began
resulting to change in morphology of the ZNRs [31].

Deposition Times.
The PL spectra of the ZNRs thin films at different growth times
are displayed in Figure 4(a). There are two PL emissions observed;
one around 385 nm and the second one around 550 nm. The blue
emission peaks also called excitonic peak emission (around 385
nm) is known to be associated with the recombination of the free
excitons of ZnO. Whereas, the PL emission peaks around ~ 550 nm
is attributed to defects such as O and Zn vacancies [33-36]. The
enhancement of the excitonic peak emission was observed when
deposition time was increased and reached a maximum at 90 min
but decreased thereafter, as illustrated in Figure 4(b). The decline
in excitonic emission, with the increase in time, could be due to
increased concentration of deep level defects [20]. This indicates
that best crystallinity can be obtained at 90 min of deposition time
which is in agreement with the XRD observation. As shown in the
PL spectra, Figure 4(a) inset, notably the excitonic peak emission
of the ZNRs shifts towards higher wavelengths (385-387 nm) with
the increase in deposition time (30-150 min). The observed red-
shift could be as a result of growth of the particles as explained
by Ostwald ripening process where large particles overtake the
growth of small particles [30, 37].

Figure 3: AFM 3-D Images of ZNRs Prepared at Deposition
Times (a) 30, (b) 90 and (c) 150 min

In order to further the study of the surface topography of the ZNRs
thin films prepared on GZO seeded glass substrate, atomic force
microscopy (AFM) technique was utilized. Figures. 3(a-c) display
3-D AFM images of ZNRs covering 500 x 500 nm² prepared at
different deposition times. They display clear changes in surface
topography as the deposition time is increased which further
confirms the observation made with the SEM images. The ZNRs
thin films prepared at 90 min showed more defined, well-aligned
and homogeneously distributed nanorods over the all surface of
the substrate. The root mean square (RMS) roughness of the ZNRs
were 4.86, 6.07 and 9.46 nm for the deposition time of 30, 90 and
150 min respectively. The observed increase in film roughness is
attributed to the increase in grain size of particles (33.34, 39.58
and 95.03 nm for 30, 90 and 150 min of growth time) [32].

Photoluminescence Analysis

Figure 4(a): Room-Temperature PL Spectra and Inset: Enlarged
Excitonic Peak Emission Spectra for ZNRs Grown at Various
Deposition Times.

The Commission International de l’Eclairage (CIE) chromaticity
image of the as-prepared ZNRs was drawn and shown in Figure
4(c). The color emission of the ZNRs prepared in the study is
described by the x, and y coordinates of CIE. The CIE diagram
confirms the findings from the PL which indicate a red shift in
emission when the deposition time progressed from 30-90 min.

UV-V is Spectral Study

The fraction of an incident light of a specific wavelength which
passes through a sample is what is referred to as transmittance. The
transmittance spectra of ZNRs grown at different deposition times
are depicted in Figure 5(a). The spectra display high transparency
in the wavelength range 500-800 nm for all the prepared samples.
The ZnO transparency property in the visible region is thought to be due to the possession of wide band gap energy [38]. The variation of transmittance with deposition time was observed. It was noted that the films revealed a decline in transmittance at a prolonged duration of deposition. High transmittance displayed at a shorter duration of growth could be attributed to a thin layer of the film formed. As the growth progresses to longer deposition time, the film becomes dense as larger and longer NRs are formed and hence reducing the % percentage transmittance. Furthermore, a red shift in absorption edges was observed as deposition time is increased from 30-150 min as depicted in Figure 5(a). The shift to a longer wavelength at a prolonged duration of growth could be due to enlargement of grains formed.

The absorption coefficient (α) is calculated from % T data using the Beer-Lambert law eq. (3):

$$\alpha = \frac{1}{d} \ln \left( \frac{1}{T} \right)$$  \hspace{1cm} (3)

The a and the incident photon energy (hν) is related by the Tauc’s formula eq. (4). In the case of direct allowed transitions such as those found in the direct band gap of ZnO, close to the band edge, a approximates to the equation. The band gap of the material is denoted as Eg.

$$\alpha h\nu = A(\nu - E_g)$$  \hspace{1cm} (4)

The nature of the band gap transition is said to be direct as could be explained by the linear nature of the plot. The extrapolation of the linear portion of the curve to the energy axis at hν = 0, gives the values of the band which was found to decrease with increase in deposition time from 2.79 to 2.01 eV for the ZNRs as shown in Figure 5(b). This phenomenon can be explained to be caused by the increase in the size of the crystallites and alteration of grain borderline arrangements during growth as confirmed by XRD results. The values of band gap energies obtained in this study agree with those reported by Ajuba et al (2010) [39, 40]. Variation in the values of band gap of the ZNRs films with deposition time offers an easy way to engineer both the structural and optical properties to suit a specific application.

**Conclusions**

ZNRs thin films were successfully produced on GZO seeded substrate by the two-step CBD technique at different deposition times while keeping growth temperature and precursor concentrations constant. XRD analysis displayed a wurtzite structure with a preferred [002] plane orientation with the NRs growing along the c-axis. Increase in crystallite sizes calculated from the Scherrer’s formula with an increase in deposition time was observed. SEM and AFM images showed a variation of surface morphologies with deposition time with well aligned NRs obtained at 90 min of growth time. The PL excitonic peak intensity was found to increase to a maximum at 90 min and decreases thereafter for a longer duration of growth due to increase in defects in the samples. The ZNRs sample obtained at 90 min was confirmed, by the analysis techniques, to possess the best structural and optical properties hence the recommended deposition time for the preparation of the nanorods by CBD on the GZO substrate.

**Declaration of Conflict of Interest**

The authors declare no conflict of interest.

**References**


