Effect of Annealing Temperature in ZnO For Photonic Applications

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Abstract: ZnO nanorods were synthesized on glass substrate by two step chemical bath deposition (CBD) method and annealed at different temperatures in argon environment for 1 hour. The structural and optical properties of the as-grown and annealed samples were investigated using X-ray diffractometer (XRD), UV-Visible-NIR spectroscopy, Raman spectroscopy and photoluminescence (PL) measurement. As grown sample has the largest crystallite size with a photonic gap of 90 nm whilst. Raman measurement shows sharp E2(H) peak typical for the wurtzite ZnO structure and PL spectra exhibit a strong UV emission peak at 380 nm for all samples. The ratio of UV to visible peak in the PL spectrum for as grown sample was the highest indicating lowest level of defects for these set of samples. This is consistent with the crystallinity of the samples. Results suggest potential of using CBD as a method of growth for synthesizing ZnO nanorods for nanophotonic devices.

1. Introduction

Zinc Oxide (ZnO) has generated great interest due to its direct wide band gap of 3.37 eV and large exciton binding energy of 60 meV with many applications including light emitting diodes [1], UV photodetectors [2], solar cells [3] and many more. In addition to that, due to its transparency and electro-optical and elasto-optical properties, ZnO is attractive for integrated photonic devices [4]. As nanotechnology blooms, investigations of optical properties of nanostructures have led to better design and control for nano scale devices.

Several techniques have been used to prepare ZnO nanostructures, such as molecular beam epitaxy (MBE) [5], chemical vapour deposition (CVD) [6], pulse laser deposition [7], sol-gel method [8] and chemical bath deposition (CBD) method [9]. However, chemical bath deposition (CBD) method have many advantages, such as low cost and low working temperature [10]. Compared to other low cost method, CBD provides a more promising option due to its large scale controllability and have shown to be superior in producing good morphology of ZnO nanorods [11]. Based on previous studies, post annealing treatment in samples prepared by CBD has been reported using air flow [12], oxygen [13], nitrogen and even in vacuum [14] environment. However, the effect of annealing under argon environment no detailed reports of the growth characteristics is available, up to our knowledge.

In this paper, the properties of ZnO nanorods that prepared by a simple chemical bath deposition method for potential nanophotonic applications was addressed. The nanorods were synthesized using the CBD method at a fixed growth temperature of 96°C for 4 hours. A thin ZnO layer was deposited by using RF sputtering prior to growth and several parameters like molarity, growth temperature, time of annealing and gas for annealing has been fixed. The growth characteristics at different annealing
temperature are analysed by scanning electron microscope (SEM) and X-ray diffraction measurements. Optical properties were measured by UV-Vis spectroscopy and photoluminescence measurements.

2. Method

Growth: Prior to growth, the glass substrates were pre-coated with 100 nm of ZnO using RF sputtering at room temperature in high purity of argon using a ZnO target with purity 99.999%. Then, all the samples except an as grown sample undergo annealing process at different temperatures of 350, 400, 500 and 600°C for 1 hour in argon environment. The rate flow for argon in a furnace is 3.0 slm. Then, all the seeded substrates were immersed into chemical solution consisting equi-molar of zinc nitrate hexahydrate and hexamethylenetetramine (HMT), dissolved in deionized water. The growth temperature was fixed at 96°C for the entire growth period of 4 hours. All samples undergo annealing for 1 hour in argon environment at different temperatures post growth.

Characterisation: The crystallinity of the ZnO nanorods was analysed from XRD measurement using a Cu Kα radiation source with wavelength of 1.5406 Å. Scherrer’s formula was then used to determine the crystallite size. UV-Visible-NIR spectrophotometer was utilized to obtain the transmittance spectra and to determine the photonic gap of the samples. Raman measurement with spectrometer Horiba Jobin Yvon HR800 with Ar⁺ ion laser as the excitation source operating at a wavelength of 514.55 nm and power of 20 mW was used to study the vibrational modes from the ZnO nanostructures. Meanwhile, photoluminescence (PL) measurement was carried out using a continuous wave He-Cd laser (325 nm, 20 mW) at room temperature to observe optical characteristics of the samples.

3. Result and Discussion

3.1 X-ray diffraction analysis

XRD spectra of the ZnO nanorods annealed at different annealing temperatures are shown in Figure 1. The as grown sample was included as reference. All peaks can be indexed to the hexagonal wurtzite structure with 2θ value of 34.4°, which is corresponding to the (002) plane. No diffraction peaks related to impurities were observed. The average particle size of all samples was calculated using the Debye-Scherer formula[15]:

\[ D = \frac{K\lambda}{\beta \cos \theta} \]  

where \( \kappa \) is a constant with a value 0.9, \( \lambda \) is radiation source wavelength, \( \beta \) is full half-maximum (FWHM) intensity and \( \theta \) is diffraction angle. The average particle size of all samples, calculated using equation (1) is approximately 48.99 nm, 46.28 nm, 43.75 nm, 41.95 nm and 44.05 nm for as grown, 350, 400, 500 and 600°C, respectively as shown in Table 1.

The lattice strain (\( \varepsilon \)) has been determined by using the tangent formula [15], whereas the d-spacing can be measured by the following relations [15]:

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

\[ d_{hkl} = \frac{1}{\sqrt{\frac{h^2 + k^2 + l^2}{3a^2}} \cos \theta} \]

where \( \beta \) is FWHM, \( d \) is interplanar distance, \( \lambda = 1.5406 \text{ Å} \) is the wavelength of the X-ray radiation used, \( \theta \) is the angle of the diffraction peak with respect to the orientation considered for calculation. The calculated values for each sample are tabulated in Table 1.

The as grown sample showed strongest intensity with smallest full-width at half-maximum (FWHM) value and largest crystallite size; indicating good crystallinity of the ZnO nanorods grown in the z-direction (growth direction). The spacing and lattice strain follows the same trend, whereby as
annealing temperature increases, both lattice strain and \(d\)-spacing increases until the annealing temperature reach 600ºC. Crystallinity starts to improve at this temperature indicating that a temperature above 600ºC is needed to improve crystallinity in samples prepared by this method of CBD. However due to the limit of annealing soda lime glass substrates, it is not possible to maintain the glass structure at higher annealing temperatures. However, as grown samples already exhibit good crystallinity without the need of annealing treatment. Preheating the substrate, as done in this work, would also affect zinc acetate decomposition and crystal growth and may explain the reduced intensity from the XRD spectrum at the \(c\)-axis orientation obtained from annealed samples [16].

![Figure 1: XRD spectra of all annealed samples in argon environment at different temperatures for 1 hour. Sample without annealing treatment also included in this measurement. Samples undergo annealing shows a polycrystalline structure whereas as-grown sample showed good crystallinity.](image)

Table 1: Growth parameters of as-grown and annealed samples at different temperatures for 1 hour in argon atmosphere.

| Temperature | 2-theta (\(\theta\)) | FWHM (°) | Average crystallite size (nm) | \(d\)-spacings (Å) | Lattice strain (\(\varepsilon\)) |
|-------------|----------------------|----------|-------------------------------|-------------------|-------------------------------|
| As grown    | 34.417               | 0.158    | 48.99                         | 2.6053            | 0.1318                        |
| A350        | 34.403               | 0.168    | 46.28                         | 2.6066            | 0.1396                        |
| A400        | 34.418               | 0.177    | 43.75                         | 2.6052            | 0.1476                        |
| A500        | 34.427               | 0.185    | 41.95                         | 2.6048            | 0.1538                        |
| A600        | 34.418               | 0.176    | 44.05                         | 2.6035            | 0.1465                        |

3.2 UV-Visible Spectroscopy analysis

The UV-Vis transmission spectra of the ZnO nanorods are shown in Figure 2. The photonic gap, the region of zero light transmission, for all samples lie between 287 and 381 nm, which is typical for samples grow by CBD [17]. The widest photonic gap belongs to as-grown sample, whereby the photonic band gap is 94 nm. A summary has been included in Table 2.

A plot of \((\alpha h \nu)^2\) vs. \(h\nu\) as shown in Figure 2(b) was used to determine the optical band gap with relation

\[
\alpha h \nu \approx (h \nu - E_g)^{m/2}
\]

where \(h\nu\) is the photon energy and \(m=1\) for a direct transition. The optical band gap was found to be 3.21, 3.24, 3.26, 3.27 and 3.27 eV for as-grown, 350, 400, 500 and 600ºC, respectively as summarized in Table 2. With the increase of annealing temperature, the red-shift of the band energy may be attributed to the increase of particle size[18].
The photonic gap provides information on the disallowed bands of wavelengths for photonic crystals and stops at the point where the threshold for photons to be absorbed is reached. This threshold gives the optical band gap of the sample and in our case, is shown to increase with increasing annealing temperature, indicating the threshold for photon absorption is higher at higher annealing temperatures. For nanophotonic devices, this would mean tuning the wavelength for photon absorption through annealing as different annealing temperatures showed different threshold (energy bang gaps) for photon absorption.

![Figure 2: (a) The transmission spectra for all samples (b) (αhv)² versus hv curves of all samples: used to determine the band gap energy of the material.](image)

| Sample   | Photonic Band Gap (nm) | Band Gap Energy (eV) |
|----------|------------------------|---------------------|
| As grown | 94                     | 3.21                |
| A350     | 90                     | 3.24                |
| A400     | 85                     | 3.26                |
| A500     | 86                     | 3.27                |
| A600     | 87                     | 3.27                |

3.3 Raman Spectroscopy

Figure 3 shows the Raman scattering spectra of the samples performed at room temperature. Spectra exhibit $E_2$ (H) mode peak around 438 cm$^{-1}$, which is typically the wurtzite hexagonal phase of ZnO and assigned to the optical phonon $E_2$ mode of the ZnO crystal [19]. A very weak and small band appeared at 331 cm$^{-1}$ attributed to the second-order Raman scattering due to the zero boundary phonons, typically called $E_{2H}-E_{2L}$ (multi-phonon process). Peaks at 380 cm$^{-1}$ also can be seen in the spectra designated to the $A_{1T}$ modes. From the spectra, $E_2$ has the strongest peak when annealed in 600°C compared to other samples which indicate sample had strong optical absorption, which is preferred for photonic applications. The broad phonon peaks located at 580 cm$^{-1}$ corresponding to $A_1$ (LO) and $E_1$ (LO) modes is nominally attributed to defect, which is likely due to oxygen and zinc interstitials in our case.
3.4 Photoluminescence Measurement

Figure 4 shows the PL spectra of the ZnO nanorods annealed at different temperatures. The spectra consist of a strong UV peak at 385 nm related to near-band edge emission and a broad deep-level emission (visible emission) peak in the visible range. The deep level emission mostly in the green and partly in the yellow and red spectral regions is generally attributed to deep level defects, such as O vacancies ($V_o$), Zn vacancies ($V_{zn}$), interstitial O ($O_i$), interstitial Zn ($Zn_i$) and extrinsic impurities [20]. Shifts in the UV peak is consistent with shifts in the calculated optical band gap energy as in Table 2.

The relative PL intensity ratio of UV emission to deep level emission for all samples, as shown in Figure 4(b) is roughly 2.25, 2.19, 1.62, 1.10 and 1.98 corresponding to as grown, 350, 400, 500 and 600°C, respectively. The highest ratio value for the as-grown and sample annealed at 600°C indicate lowest level of point defects in these samples. As temperature is introduced it is likely these defects move deeper into the structure, hence showing increased emission in the visible spectrum. However, 600 °C seems to be the recrystallization temperature for these samples as these defects are significantly reduced at this temperature. This result is consistent with the XRD analysis indicating increased crystallinity as these point defects are reduced.

4. Conclusion

ZnO nanorods were successfully grown on glass substrates by a simple chemical deposition method and undergo annealing process at different temperatures in argon environment for 1 hour. Sample annealed at 600°C shows the best sample for photonic applications with strong optical absorption as observed in the Raman spectra and lowest deep level associated defects despite reduced crystallinity compared to as-grown samples. Results also suggest 600°C as the minimum temperature for recrystallization in such
a structure and annealing above this value is needed for ZnO nanorods prepared by CBD for potential nanophotonic applications.

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