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NONLINEAR OPTICAL APPLICATIONS OF CHEMICAL METHOD GROWN HIGH DENSITY ZNO NANORODS

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ABSTRACT:
In this work we demonstrate the nonlinear optical applications and the growth of high density ZnO nanorods by using drop casting of the seed layer calcinated at a low temperature of 132°C. Chemical bath deposition (CBD) method is used to grow the nanorods. X-ray diffraction analysis, Field Emission Scanning Electron Microscopy is performed for the structural and morphological characterization of the nanorods. The average diameter and length of nanorods are found to be 33 nm and 270 nm respectively. The bandgap of the material is estimated to be 3.2eV from the UV-Visible absorption spectroscopy. A domestic induction heater is used for the aforementioned low temperature calcination process. As such CBD is one of the most simple and cost effective methods. The use of induction heater calcinated drop casting seed layer further reduces the required capital investment to grow high density ZnO nanorods.

INTRODUCTION :
ZnO nanorods are promising for various applications such as, gas sensors [1], UV detector[2], second harmonic generation(SHG) and multi photon luminescence [3,4], photovoltaic cells [5], photocatalysis[6] etc. ZnO nanorods have been grown by several methods like chemical vapor deposition, pulse laser deposition, vapor-liquid-solid deposition, chemical bath deposition (CBD) methods etc. [7]. The CBD method has an advantage over other methods due to its simplicity. It does not need any sophisticated equipment, involves low temperature processing steps and is a low cost deposition technique [8]. However to grow high density ZnO nanorods on various substrates, a seed layer is usually required [7]. A variety of techniques including thermal deposition, radio frequency magnetron-sputtering, spin coating and drop casting are applied to prepare ZnO seed layers on substrates [9]. Amongst these, the drop casting technique is simple and both time and cost-effective. In this method zinc acetate and ethanol are used as the precursors. Multiple layer coatings are prepared on the substrate by drop casting a solution of these precursors. Finally the seed layer is formed after calcination of the coating. This calcination is generally done at temperature of ~300oC by the use of conventional laboratory furnace. In this work we have demonstrated that seed layer calcinated at low temperature of 132oC by the use of a domestic induction heater can also be used for the growth of high density ZnO nanorods, thereby making this method much more cost effective.

EXPERIMENTAL DETAILS :
Material Synthesis
The ZnO nanorods are grown on glass substrates by a two-step process. In the first step the seed layer is grown by a drop casting method [10]. In this method 0.022gm of zinc acetate dihydrate (C4H6O4Zn.2H2O) is mixed with 20ml of absolute ethanol to obtain a 5 mM solution. Then 0.06ml of this solution is uniformly spread over the glass substrate of area 16.5cm2 followed by drying in hot air for 10 minutes. This process is repeated on the same substrate for four times. Then the samples are heated in an indegeneously built domestic induction heater based heating system to form the ZnO seed

layer. The saturation temperature offered by this system at minimum (120 W) and maximum (2100 W) power of indiction heater are found to be 74°C and 132°C respectively on the top surface of the sample. We performed the calcinations at 132°C for one hour to get the ZnO seed layer.

In the second step of the process ZnO nanostructures are grown using CBD method on this seed layer. For this 0.15gm of Zinc nitrate hexahydrate (Emplura) is mixed with 25ml of distilled water to prepare a 20mM zinc nitrate($Zn(NO3)2$) solution. Then 0.8M of NaOH solution is prepared by mixing 0.81gm of NaOH (Himedia) and 25ml of distilled water followed by stirring. Then 25ml of both zinc nitrate and NaOH solutions are mixed slowly to prepare 50ml of mixture solution and this mixture is then stirred for 5 minutes. This solution is heated to 70°C and the previously prepared samples with seed layers are submerged in the mixture solution for two hours with slow stirring by maintaing this temperature. After this the substrates are removed from the solution, washed with distilled water and dried with hot air.

Characterization

The morphology of samples is then characterized by Field Emission Scanning Electron Microscopy (FESEM) using a Carl Zeiss Sigma system. The X-ray diffraction XRD analysis is done using a Bruker D8 Advance X-ray diffractometer to verify the crystal structure and phase. To find the band gap, UV-VIS absorption spectroscopy is done using Lambda 900 spectrophotometer of Perkin Elmer.

RESULTS AND DISCUSSION

FESEM image of the ZnO nanorods grown on the glass substrate with seed layers is shown in Fig.1. From this figure growth of high density ZnO nanorods is quite clear. The average diameter and length of the ZnO nanorods are 33 nm and 270 nm respectively (aspect ratio ~ 8).This value is found to be similar to the value reported by Chan et al. in ZnO nanorods grown by CBD technique with conventional laboratory furnace calcinated drop casting seed layer [11]. The ZnO nanorods are found to be well oriented.

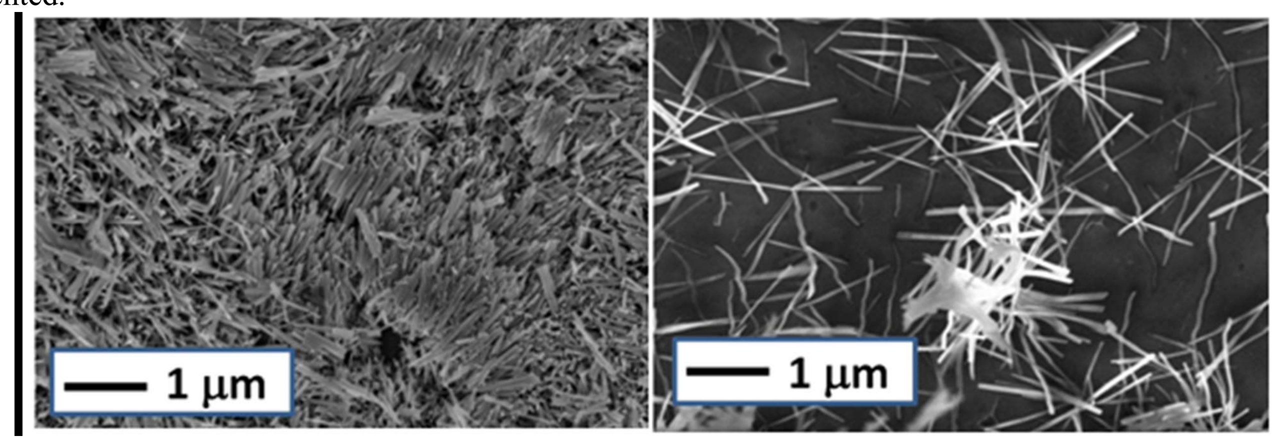

FIGURE 1. FESEM image of the ZnO nanorods grown on substrates with seed layer (a) and without seed layer (b).

For comparative study we have also grown ZnO nanorods on a glass substrate containing no seed layer by following second step of experimental section. The FESEM image of the ZnO nanorods grown on glass substrate without any seed layer is shown in Fig. 2. In this case the density of ZnO nanorods are

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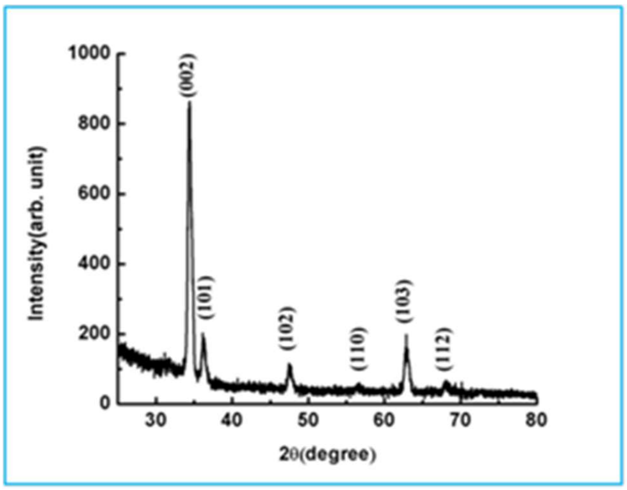
found to be very less and randomly oriented. Comparison of Fig. 1 and Fig. 2 makes it clear that the seed layer has facilitated the growth of higher density nanorods.

The XRD peaks of the ZnO nanorods grown on seed layer are shown in Fig. 3. The peaks at 2θ angles of 34.4o, 36.1o, 47.4o, 56.7o, 62.8o, and 68.0o corresponds to (002), (101), (102), (110), (103) and (112) hexagonal wurtzite ZnO [ZnO: JCPDS Card No. 36-1451]. The departure from the intensity pattern expected from the powder diffraction file indicates a preferred c-axis oriented growth of the ZnO nanostructures, consistent with the FESEM data in Fig. 1.



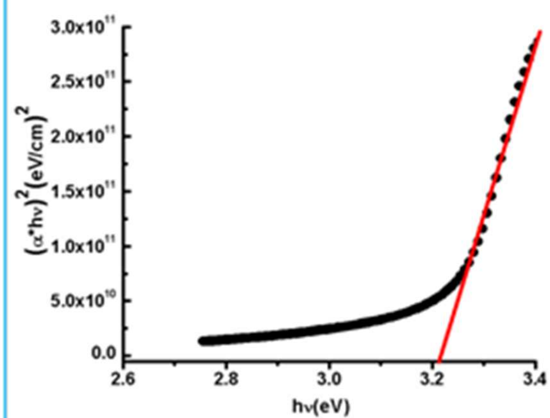


FIGURE 2. XRD data from ZnO nanorods grown on the seed layer (a) and the plot of $(\alpha h\nu)^2$ vs. hν for ZnO nanorods

The Tauc plot i.e. (αhν)2 vs. hν graph for the ZnO nanorods as estimated from UV-Visible absorption spectroscopy is shown in Fig. 4. The absorption coefficient (α) is related to the incident photon energy hν as:

$$\alpha = [k(h\nu\text{-}Eg)n/2]/h\nu \quad (1)$$

Where k is a constant, Eg is the optical band gap and n is equal to 1 for direct band gap material such as ZnO [12]. From the straight line fitting of this graph, the band gap of ZnO nanorods film is found to be 3.2 eV. This value is found to be similar with the result published by Zhang et al. [6]. Therefore all these results confirm the formation of growth of high density ZnO nanorods of usual properties.

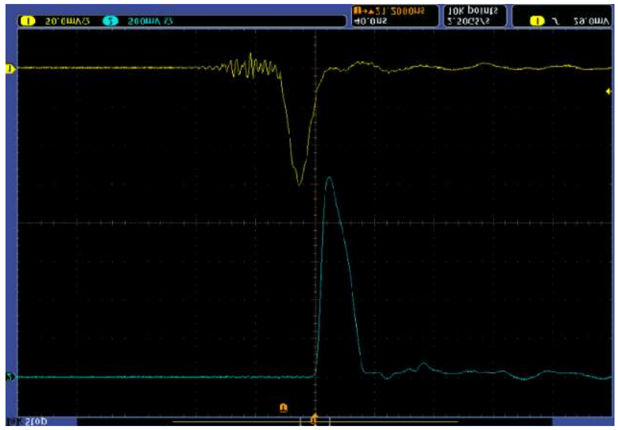


FIGURE 3. Second Harmonic Generation with the ZnO nanorods grown on the seed layer.

High density ZnO nanorod growth using CBD method in conjunction with a drop casted seed layer has been demonstrated by various authors [11-15]. In all these works the seed layer is calcinated at temperature > 300 oC. This temperature is much higher than our case. Further it is to note that in all these works the growth of the seed layer is done by the use of conventional furnace. In this work we also have demonstrated that a domestic induction heater can be used for this purpose. This type of heating system is extremely cheap. For our case it is about $50. Domestic induction heater is also an efficient and stable heating device, so the reported method for the growth of high density ZnO nanorods is much more cost effective because of lower capital investment. These materials can be found to be promising for various applications like SHG, gas sensors, UV lasing, photovoltaic cells, photocatalysis etc.

CONCLUSIONS :

In this work high density ZnO nanorods are grown by a CBD technique using drop casting to form a seed layer in a calcination time of one hour at temperature 132oC. We have used a domestic induction heater for the calcination of the seed layer. XRD analysis of the sample confirms the formation of ZnO and FESEM characterization reveals that the nanorods have an average diameter of 33 nm and length of 270 nm respectively. The band gap of ZnO nanorods is found to be 3.2 eV. Unlike a conventional laboratory furnace, a domestic induction heater which significantly reduces the capital investment requirement for the growth of high density ZnO nanorods is a very cost effective alternative.

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