5.1 Introduction

Geometry and dimensionality are indispensable factors in determining the properties of nanomaterials, and control over the size and shape is of great importance with regard to specific nanoscale applications. Recently, nanomaterials in the form of nanoparticles, nanorods, nanowires and nanobelts have received considerable attention due to their interesting physical and chemical properties and extensive applications in the fields of electronics and optoelectronics [Xia et al., 2003; Samuelson, 2003]. Especially, one-dimensional nanostructures such as nanowires and nanorods are regarded as promising candidates for nanodevice assembly and applications in nanoelectronics, photonics, mobile miniaturized devices, portable rechargeable batteries, coatings, data recording media, gas sensing, field emitting devices and dye sensitized solar cells [Zu et al., 1997; Kong et al., 2001; Krunks et al., 2008; Li et al., 2004; Lakshminarasimhan et al., 2008].

Among different oxide semiconductor materials, ZnO has the richest family of nanostructures. ZnO exhibits diverse and versatile morphologies in comparison with any other material known today [Wang et al., 2004]. ZnO is reported to crystallize and grow into diverse morphologies such as nanorods, nanoplates, nanoflowers, hollow sphere, fibers, nanowires, nanobelts, nanocombs, nanospirals, tetrapods and nanorings [Wang et al., 2004; Wu et al., 2005; Maity et al., 2005; Liaoa et al., 2005; Liu et al., 2005; Dem’yanets et al., 2006; Liu et al., 2006; Kou et al., 2006; Liang et al., 2006; Sui et al., 2006]. ZnO nanostructures are promising building blocks for nanoelectronic and nano-optoelectronic devices. Research on one-dimensional (1D) nanostructures of ZnO has attracted a great attention due to their unique and novel applications in blue-UV light emitters [Bao et al., 2006], photodetectors [Law et al.,
Research on one-dimensional ZnO was first inspired by the discovery of oxide nanobelts in 2001 [Wu et al., 2002]. One-dimensional nanostructures of ZnO can be synthesized by either physical vapour deposition methods at high temperature (600 °C) or chemical approaches at low temperature (70 °C) on a wide range of substrates without using sophisticated or expensive equipments. Different techniques such as chemical vapour deposition (CVD) [Wu et al., 2002], physical vapour deposition (PVD) [Yan et al., 2003], sol-gel technique [Ghosh et al., 2007] and hydrothermal method [Dem'yanets et al., 2006] have been used for the synthesis of ZnO nanostructures. Recently, Hu et al. reported the optical properties of ZnO nanorods and whiskers synthesized by the oxidation of ZnS powder at 1300 °C [Hu et al., 2002]. Dai et al. [2003] reported the optical and electrical properties of ZnO nanowires synthesized by CVD method. Moreover, different types of substrate such as alumina [Wang et al., 2004], silicon [Umar et al., 2005; Jeong et al., 2005] and steel [Umar et al., 2006] have been used to grow ZnO nanostructures. However, there are only a few reports on the study of the synthesis and physical properties of thin films composed of ZnO nanorods.

Electron transport property of nanorods is reported to be more attractive compared to that of nanoparticles for certain applications [Lupan et al., 2010]. Huang et al. [2001] observed lower lasing threshold value for ZnO nanowire arrays at room temperature in comparison with ZnO nanoparticles. Surfaces, grain boundaries and interfaces play a crucial role in tuning the electronic and optical properties ZnO nanostructured thin films [Pasquier et al., 2006; Kopidakis et al., 2005]. It is expected that a direct conduction pathway from the point of electron–hole pair generation to the collection electrode would significantly improve the electron transport efficiency [Kopidakis et al., 2005; Kamat, 2007]. In this regard, one-dimensional ZnO nanostructures made up of nanorods and nanowires show attractive characteristics compared to nanoparticulate films for optoelectronic devices. This is because one-dimensional nanostructured ZnO have high aspect ratio and they provide direct pathway for photogenerated charge carriers compared to nanoparticulate film [Kamat, 2007; Law et al., 2005]. One-dimensional nanostructure can help improve electron transport by avoiding the particle-to-particle hopping that occurs in the particulate film network. Law et al. [2005] found that the electron diffusion coefficient in nanowires is several hundred times larger than that in nanoparticle films. Therefore, an
investigation of structural, optical and transport properties of nanostructured ZnO films composed of nanorods is of critical importance for the development of novel devices.

In the present chapter 5, the author reports the optical and electrical properties of films composed of zinc oxide nanorods synthesized by thermal oxidation of nanostructured zinc films deposited on glass substrates without the help of any catalyst. The nanostructured zinc films were deposited on glass substrates at a nitrogen pressure of $\sim 4 \times 10^{-4}$ mbar at room temperature which is a method similar to the gas evaporation technique [Koshy and Khadar. 2011]. The photoluminescence (PL) spectra of films of ZnO nanorods showed negligible defect emission when compared with the UV emission. Micro-Raman measurements on the films of ZnO nanorod samples showed a peak at 582 cm$^{-1}$ with low intensity which corresponds to the defect mode such as oxygen vacancies and zinc interstitials. UV photodetection properties of film samples composed of ZnO nanorods were also studied.

5.2 Experimental details

Nanostructured thin films of zinc were deposited on the soda lime glass substrates by thermal evaporation of zinc granules. The glass substrates were cleaned using a standard procedure (Chapter 2, section 2.2) before deposition. Depositions of the nanostructured films were carried out not at high vacuum but at an appreciably high pressure of nitrogen gas of $4 \times 10^{-4}$ mbar. Thermal oxidation of the samples was done in a furnace at 500 °C in air for one hour (sample code, S1) and two hours (sample code, S2).

The crystal structure and crystallinity of the film samples were investigated using a Brucker AXS D8 advance x-ray diffractometer equipped with Kristalloflex 780, KF.4KE, X-ray source ($\lambda \sim 1.54 \text{ Å}$). The evolution of morphology of the film samples was examined using atomic force microscopy (AFM) using Digital Instruments Nanoscope E in contact mode and JEOL JSM-5610 Scanning electron microscope (SEM). The detailed microstructure of the nanostructured ZnO film samples was studied using a JEOL 2100F Transmission electron microscope. The films of ZnO nanorods were mechanically scrapped and sonicated in ethanol and deposited on carbon-coated copper grids for TEM characterization. The photoluminescence spectra from the film samples were recorded using a Hitachi FL-
700 spectrophotometer using an excitation wavelength of 300 nm. Micro-Raman measurements on the samples were performed using Labram HR 800 spectrometer and using 488 nm line of argon ion laser. For photoconductivity measurements, silver co-planar electrodes were deposited at a separation of ~1.5 mm on the surface of the films. For photoconductivity studies, a 1000 W xenon lamp (Oriel instruments, USA) was used as the source of light. Light from the xenon lamp was passed through a column of water to remove heat radiations. Photocurrent measurements were carried out over the wavelength range from 200-800 nm. The photo response transients were measured using a Keithley model 2400 source meter and a Tektronix digital storage oscilloscope.

5.3 Results and discussion

5.3.1 X-ray diffraction studies (XRD)

Fig. 5.1 (a) and (b) shows the x-ray diffraction (XRD) patterns of nanostructured zinc oxide film sample, S1 oxidized at 500 °C for 1 hr and those of S2 oxidized at 500 °C for 2 hr respectively. The XRD pattern of the film sample S1 showed a strong diffraction line at 2θ value of 34.4° corresponding to the (002) reflection along with weak peaks at 31.2° and 36.3° which correspond to reflections from (100) and (101) planes of ZnO (ICDD file 03-0888). The XRD pattern of the film sample S2 showed similar pattern except that the intensity of (100) and (101) reflections increased in comparison with that of the corresponding peaks of the film sample, S1. The high intensity of (002) reflection in the XRD pattern of film sample S1 and S2 when compared with the intensities of other two reflections suggests that the films had preferential orientation (Table 5.1). The XRD patterns of film sample S1 and S2 showed maximum intensity for (002) reflection while in the XRD pattern of bulk ZnO, (101) reflection has maximum intensity (ICDD file 03-0888). This indicates that the present film samples had preferential orientation along (002) plane [Hung et al., 2003; Peng et al., 2006].
Table 5.1 Oxidation temperature and texture coefficient of film samples S1 and S2.

<table>
<thead>
<tr>
<th>Oxidation temperature (°C) and duration</th>
<th>Relative intensity</th>
<th>Texture Coefficient (TC (002))</th>
</tr>
</thead>
<tbody>
<tr>
<td>hkl</td>
<td>Standard</td>
<td>Observed</td>
</tr>
<tr>
<td>500 °C for 1 hr</td>
<td>100</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>002</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>101</td>
<td>100</td>
</tr>
<tr>
<td>2.735</td>
<td></td>
<td></td>
</tr>
<tr>
<td>500 °C for 2 hr</td>
<td>100</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>002</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>101</td>
<td>100</td>
</tr>
<tr>
<td>2.232</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.1: XRD pattern of film samples a) oxidized at 500 °C for 1 hr, (Sample S1) and b) oxidized at 500 °C for 2 hr, (Sample S2).
5.3.2 Scanning Electron Microscopy studies (SEM)

Fig. 5.2 (a)-(b) show the SEM images of film samples S1 and S2. The SEM image (fig. 5.2 (a)) of the film sample, S1 shows agglomerated particles while the film sample S2 shows nanorods (fig. 5.2 (b)). The length of nanorods in fig. 5.2 (b) is in the range 1-2 µm. From the above observations, it is concluded that the morphology of the deposited films undergoes a drastic change from a uniform and granular structure to one dimensional nanorod with increase in duration of oxidation.

Figure 5.2: SEM image of nanostructured ZnO films oxidized at a) 500 °C for 1 hr, (Sample, S1) and b) 500 °C for 2 hr, (Sample, S2).
5.3.3 Atomic Force Microscopy studies (AFM)

Fig.5.3 (a)-(d) shows AFM images of film samples S1 and S2. The AFM image of the film sample S1 (Fig.5.3 (a)) exhibit spherical particles of agglomerated grains. The AFM image of the nanostructured ZnO films, S2 shows rods (fig. 5.3(b)). Fig.5.3 (b) - (d) show the AFM image of film sample S2 at different magnifications. Large numbers of nanorods are observed. The length of ZnO nanorods measured from the figure is around 1-3 μm. From the above observations, it is clear that morphology of the present film samples depend strongly on the time duration of oxidation. When the duration of oxidation is 1 hr, nanoparticles are observed (fig.5.3 (a) Further increase in the oxidation time to 2 hr resulted in the increase in the number of nanorods (fig.5.3 (b)-(d)).

Longer oxidation time provides more thermal energy to individual grains. Lin et al. [2005] reported that high temperature can stimulate the migration of grain boundaries and cause the coalescence of neighbouring grains during the annealing process. Fang et al. [2005] indicated that, at high temperature, more energy would be available for the grains to move so that they may grow larger at high temperature by merging of individual grains in order to lower the surface energy. In the present film samples S2, large thermal energy available stimulated the coalescence of neighbouring grains in order to lower the surface energy of the individual grains and as a result nanorods were formed.
Figure 5.3: AFM images of ZnO film oxidized at a) 500 °C for 1 hr b) 500 °C for 2 hr c) 500 °C for 2 hr (different magnification) and d) 500 °C for 2 hr (different magnification).
5.3.4 Transmission Electron Microscopy studies (TEM)

Figure 5.4: a) TEM image of films of ZnO nanorods formed at 500 °C duration 2hr 
b) SAED pattern of ZnO nanorods c) HRTEM image of ZnO nanorods 
and d) Corresponding FFT Pattern
Fig. 5.4 (a) shows low-magnification TEM image of the ZnO nanorods. The measured diameter of ZnO nanorods is 25 nm and length about 1-1.5 \( \mu \text{m} \). Fig. 5.4 (b) shows the selected area diffraction pattern (SAED) of ZnO nanorods. The diffraction pattern is spotty indicating the preferred orientation in the film samples. Similar patterns were reported by several authors in the case of ZnO nanorods and they attributed the spotty nature of the patterns to the preferred orientation along (002) plane [Umar et al., 2007; Cao, 2004]. The regularly spaced spot pattern of SAED indicates the single crystalline nature of the nanorods [Choopun et al., 2010]. Fig. 5.4 (c) shows the HRTEM image of ZnO nanorods. Fig 5.4 (d) shows the corresponding FFT image patterns. The interplanar spacing (d) between two adjacent planes measured is 0.26 nm. This spacing corresponds to the (0002) plane of ZnO [Giri et al., 2011; Yang et al., 2008]. This confirms that the growth direction of ZnO nanorods is along (0001) direction.

To understand the growth of ZnO, it is necessary to study its growth mechanism. Basically, the growth of nanostructured films occurred in two stages, viz. nucleation and growth. The importance of temperature in the growth of ZnO nanostructures could be understood from the basic theory of crystal nucleation and growth [Ahsanulhaq et al., 2007]. In the present experiment the nanostructured Zn films are oxidized at 500 °C for 1 hr. As the oxidation process progressed, zinc nanograins reacted with oxygen forming ZnO nanograins [Guo et al., 2008]. In the second stage i.e. when the oxidation time is increased ZnO nanograins coalescence to form ZnO nanorods (fig 5.2 (b)).

From the TEM and SAED Pattern of ZnO nanorods, it was observed that ZnO nanorods grew preferentially oriented along (0001) direction. Thermodynamically, growth takes place along the low surface energy plane in order to reduce the surface energy [Guo et al., 2008]. In the case of ZnO nanorods, the growth is usually observed along the (0001) direction, as the growth velocity along this plane is faster than any other direction [Umar et al., 2006]. Another explanation for the growth of ZnO nanorods along (0001) direction can be given as: The structure of ZnO, can be described as a number of alternating planes composed of tetrahedrally coordinated O\(^{2-}\) and Zn\(^{2+}\) ions, stacked alternately along the c-axis. ZnO is a polar crystal and hence has positively charged Zn-(0001) terminated surfaces which are chemically active (maximum surface energy) and negatively charged O-(000\(\overline{1}\)) polar surfaces which are
inert (minimum surface energy) for the growth of nanostructures resulting in a normal dipole moment [Umar et al., 2006; Umar et al., 2007; Cao, 2004; Peng et al., 2006]. If the surface charges are uncompensated during the growth as the oxidation time increases, the spontaneous polarization induces electrostatic energy due to the dipole moment. However, in order to reduce the electrostatic energy, rods are formed along [0001] direction which would minimize or neutralize the overall dipole moment [Cao, 2004]. Therefore, the growth along the [0001] direction is the fastest and dominant one compared to other growth direction.

5.3.5 Micro-Raman spectroscopy

Fig. 5.5 shows the Raman spectra of film sample S1 and S2. Four optical modes have been observed in the spectra of films samples S1 and S2 around 331, 380, 437 and 582 cm\(^{-1}\). The Raman mode at 437 cm\(^{-1}\) originated from the E\(_2\) (high) mode, which is a typical Raman active branch of hexagonal ZnO of wurtzite phase. This peak corresponds to the oxygen vibration in Zn-O bond. The peak at 331 cm\(^{-1}\) can be assigned as 2-E\(_2\) (M) which arises from the zone boundary [Cusco et al., 2007]. The weak peak at 582 cm\(^{-1}\) corresponds to the E\(_1\) (LO) modes which is associated with oxygen vacancies in ZnO [Alim et al., 2005]. The low intensity of E\(_1\) (LO) in the Raman spectra is due to the negligible presence of structural defects such as oxygen vacancies, zinc interstitials and free carriers and impurities in the grown material (fig. 5.5) [Umar et al., 2007].

Figure 5.5: Micro-Raman spectra of a) film sample oxidized at 500 °C for 1 hr and b) film sample oxidized at 500 °C for 2 hr
Fig. 5.6 shows the photoluminescence spectra of film sample S1 and S2. A strong peak at 380 nm in the UV region is observed for S1 and S2. The full width half maximum (FWHM) of the peak at 380 nm is measured to be around 12 nm for both samples. No peak is observed in the visible region. The intensity of UV emission of film sample S1 is higher than that of S2. It is commonly known that room temperature PL spectrum of ZnO usually shows three major peaks: one near band-edge UV emission peak centered at 380 nm (3.2 eV) and other two visible emissions localized in green and red region corresponding to defect emission [Liu et al., 2004]. Zhang et al. [2003] reported a peak around 380 nm in the PL spectrum of ZnO nanorods prepared by CVD method and attributed it to the near band edge emission. Jie et al. synthesized ZnO nanorods by thermal evaporation and observed the presence of a strong ultraviolet (UV) band around 3.36 eV (380 nm) and a broad green emission peak around 2.5 eV (510 nm) [Jie et al., 2005; Jie et al., 2004]. They attributed the peak at 3.36 eV to near band edge emission and peak around 2.5 eV to defect emission corresponding to oxygen vacancies. In the present film samples S1 and S2, the peak observed around 380 nm can be attributed to the near band edge emission. The near-band-edge emission originates due to the recombination of free excitons through an exciton-exciton collision process [Wang et al., 2005; Jie et al., 2005]. In general, it is known that the green emission in the PL spectra of ZnO is caused by structural defects, oxygen vacancies, interstitials of zinc, impurities, etc. The absence of emission in the visible region (green region) in the present films samples suggests that the concentration of defects such as oxygen vacancies and zinc interstitials are negligible. For bulk ZnO crystals, strong ultraviolet emissions were observed at very low temperature (~10 K), while the intensity of the emissions was found to decrease rapidly with the increase of temperature due to the thermal quenching effect [Bagnall et al., 1997]. It was therefore difficult to observe UV light emission from bulk ZnO at room temperature. Two factors such as quantum confinement and crystalline quality are responsible for the enhancement in UV emission intensity at room temperature for nanostructured ZnO thin films of present film samples [Bagnall et al., 1997]. Several authors have [Bagnall et al., 1997, Bagnall et al., 1998] demonstrated that the improvement of crystal quality (decrease of impurities, and structure defects such as oxygen vacancies) can cause a strong near band edge emission (NBE) emission.
detectable at room temperature. In the present study, the spotty SAED pattern (Fig. 5.4 (b) suggest that ZnO nanorods are single crystalline which indicates low density of structural defects (Umar et al., 2006). The low density of structural defects is the cause of high intensity UV emission in the PL spectrum of present study (Fig. 5.6). On the other hand, quantum confinement effect and large surface-to-volume ratio related to the nanostructures is an important factor that can cause an increase in the UV emission intensity of these film samples at room temperature.

![Figure S.6](image_url)

**Figure 5.6:** Room temperature photoluminescence spectra of a) films oxidized at 500 °C for 1 hr, (Sample S1) and b) films oxidized at 500 °C for 2hr, (Sample S2).

### 5.3.7 Photoconductivity studies

Fig. 5.7 shows the photocurrent spectrum of films composed of ZnO nanorods over the wavelengths ranging from 200 to 800 nm. Only a feeble photocurrent was observed in the visible region from 800 to 450 nm but the current showed a sharp increase below 400 nm indicating that the ZnO nanorods are UV sensitive.
Figure 5.7: Photocurrent spectra of films sample S2

Figure 5.8: a) Photoresponse of films sample oxidized at 500 °C for 1 hr (Sample, S1) and b) Photoresponse of film sample oxidized at 500 °C for 2 hr (Sample, S2) to UV light

Fig. 5.8 (a) and (b) shows the rise and fall of photocurrent of films samples, S1 and S2 in response to turn-on and turn-off of the UV illumination from a xenon lamp. The ratio of maximum photocurrent to dark current (photocurrent gain) was found to be of the order of $5 \times 10^4$ for film sample oxidized at 500 °C for 2 hr, (S2) and $10^3$ for film sample oxidized at 500 °C for 1 hr, (S1) (Table 5.2). The value of film sample S2 is comparable to the reported values for films with nanorod morphology. Ghosh et al. [2010] reported a photocurrent gain of 58 for ZnO thin films prepared by sol-gel technique and $10^6$ for nanostructured ZnO thin films prepared by RF Magnetron sputtering. Mridha et al. [2008] reported a photocurrent gain of 163 for pellets of ZnO
nanoparticle prepared by chemical method. Bera et al. [2009] reported photocurrent gain of \( \sim 9 \times 10^4 \) for ZnO nanowires prepared by aqueous chemical growth via sol-gel technique. In nanoparticulate films, conduction takes place by hopping of charge carriers, however in the case of ZnO nanorods, electron transport takes place by direct transfer of charge carriers without recombination. During the hopping process, electrons will be trapped at the recombination centres while in nanorods due to the long conduction path the chance of recombination is minimized due to which the charge generated because of light illumination will reach the collection electrodes [Law et al., 2005].

Another interesting observation is the low dark current and high photocurrent for films of ZnO nanorods of the present film samples (Table 5.2). For a good light sensor, low dark current is desirable. The reason for the low dark current can be attributed to the space charge limited current (SCLC) in ZnO nanorods. The low dark current is due to the creation of surface depletion layer in ZnO nanorods where the large surface-to-volume ratio will cause the electrons to be on the surface [Bera et al, 2009; Li et al., 2004]. The mobility of electrons in the nanostructured films samples of ZnO is inhibited in the dark due to oxygen adsorption mechanism from the atmosphere. The width of the surface depletion region was \( \sim 69 \) nm for ZnO nanowires [Liao et al., 2008]. Therefore, the present films of ZnO nanorod (\( \sim 25 \) nm in diameter) will be fully depleted in the air, and the free carrier concentration will be very low. The high photocurrent observed is due to the release of large number of electrons from the surface when a light corresponding to the band gap of ZnO is illuminated on the samples [Bera et al., 2009]. Several groups made use of the high photocurrent and low dark current of ZnO nanorods for different applications. In addition, they demonstrated that it is also possible to create highly sensitive electrical switches by controlling the photoconductivity of ZnO nanowires. For e.g. Yang and co-workers [2008] found that the conductance of ZnO nanowire was extremely sensitive to UV light exposure. The light induced insulator-to-conductor transition enabled them to reversibly switch nanowires between OFF and ON states. In a typical electrical measurements on ZnO nanowires indicated that they were essentially insulating in the dark, with a resistivity of 3.5 M\( \Omega \) cm\(^{-1} \) [Kind, 2002]. When these nanowires were exposed to a UV light source with wavelength below 400 nm, their resistivity was instantly reduced by 4 to 6 orders in magnitude. In addition to their
high sensitivities, these photoconductive nanowires exhibited excellent wavelength selectivity. Therefore these highly sensitive photoconducting films of nanorods with low dark and high photocurrent can serve as a very sensitive UV-light detector in many applications.

**Table 5.2** Photocurrent, dark current and photocurrent gain, rise and decay time of films of ZnO nanorods

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Photo current ($I_{light}$)</th>
<th>Dark current ($I_{dark}$)</th>
<th>Photogain ($I_{light}/I_{dark}$)</th>
<th>Rise time ($T_r$)</th>
<th>Decay Time ($T_d$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S2</td>
<td>0.005 A</td>
<td>0.9 x 10^{-6} A</td>
<td>~5.5 x 10^4</td>
<td>15 s</td>
<td>170 s</td>
</tr>
<tr>
<td>S1</td>
<td>0.0015</td>
<td>0.5 x 10^{-6} A</td>
<td>~3 x 10^3</td>
<td>10 s</td>
<td>150 s</td>
</tr>
</tbody>
</table>

5.4 Conclusion

In summary, nanostructured films composed of ZnO nanorods were synthesized via thermal oxidation of Zn on glass substrate without the use of any catalyst. Detailed structural characterizations affirmed that the products were highly crystalline. The presence of the E$_2$ (high) mode around 437 cm$^{-1}$ in the Raman spectra and a sharp and strong UV emission at 380 nm in the room temperature photoluminescence (PL) spectra corroborate that the nanorods obtained had good crystal quality with excellent optical properties. The photoconductivity measurements indicated that the obtained ZnO nanorods were highly UV photosensitive and photosensitivity was much higher than that of nanoparticulate films.