DEPOSITION AND CHARACTERIZATION OF ZnO NANONEEDLES BY FACILE SOLUTION PROCESS

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ABSTRACT

ZnO nanoneedle clustered thin film with individual needles of length of 1000-1500 nm and diameter of around 100-200 nm were deposited on top of ZnO buffer layer coated indium doped tin oxide (ITO) glass substrate and quartz substrate by a facile solution process which is both cheap and has a low thermal budget. The microstructure of the as deposited thin films were characterized by scanning electron microscopy (SEM), whereas the x-ray diffraction (XRD) was used to determine the crystal structure in these nanoneedles. The optical characteristics of the thin films were obtained by determining the optical transmittance of the films at room temperature. The ZnO nanoneedle thin films had a bandgap of about 3.21 eV. The photoluminescence (PL) spectra obtained at room temperature confirmed the presence of defects related luminescence characterized by the broad PL peak centered at 2.1 eV.

Keywords: ZnO, Nanoneedle, Thin Film, SEM, PL

1. INTRODUCTION

One-dimensional ZnO nanostructures are technologically very important due to their potential application in various sensors, optoelectronic devices [1-5]. The ZnO one-dimensional nanosystems could be used as both active and passive elements in nanoelectronic circuit, which could provide direct path for the flow of carriers. The piezoelectronics property of the ZnO 1d nanostructures could also be utilized for energy harvesting where, power could be generated by simple application of stress on the nanosystems [6, 7]. Owing to the easy availability, low cost and ease of deposition of the ZnO one-dimensional nanosystem onto a wide range of substrates, they prove to be a viable option for the electronic industry to replace the traditional electronics towards the goal of transparent, flexible electronics [8-10], which is more suitable for modern applications under harsh working condition. In this communication, we report on the deposition and characterization of ZnO one dimensional nanoneedle cluster thin film by a simple solution process that is both facile, low cost and has a low thermal budget. The films were deposited on a ZnO buffer layer coated ITO coated glass for potential application as electrode in dye-sensitized solar cells. SEM was utilized to observe the microstructure of the deposited thin films. The crystal structure and orientation was studied by XRD (using the Cu Kα line of wavelength λ = 1.54 Å). The optical characteristic of the film was studied by measuring its transmittance spectra at room temperature using an UV-VIS-NIR spectrophotometer in the wavelength range of λ =300-800 nm. The transmittance versus wavelength data was used to compute the optical absorption coefficient of the ZnO nanosystem and hence its bandgap was also obtained. The PL spectrum of the ZnO nanoneedle thin film was obtained using a dual channel lock-in amplifier.

2. MATERIAL AND METHOD

ZnO nanoneedle cluster thin film was deposited by a facile solution process; onto an ITO coated glass substrate (Sigma Aldrich) of sheet resistance of 25 Ω/sq and fused silica substrate. Prior to deposition, the ITO coated glass and fused silica substrates were subject to rigorous cleaning process. Firstly, substrates were rinsed in deionized distilled water and then subject to ultrasonciation in an ethanol bath. This process removed any grease or dirt on the top of the substrate. These cleaned substrates were used for the deposition of the ZnO nanoneedle cluster thin films. In the first step, a 50 nm thin ZnO buffer layer was deposited by wet chemical process. In this step, 0.4M zinc acetate was dispersed in ethyl alcohol and 1:1 molar ratio of diethanolamine was added to it and stirrer continuously in a magnetic stirrer

set at 400 rpm for 2h until a clear solution was obtained. Then the cleaned substrate was dipped into the solution (under continuous stirring) five times, for 10 minutes per dip. The temperature of the bath was set at 323K for the whole deposition process. By this dip coating process, a transparent thin ZnO layer of about 100 nm thickness was deposited onto the substrate. The films were then removed and dried at 473K in open air. This ZnO layer also acted as a buffer layer on the ITO coated glass and assisted in the one-dimensional growth of ZnO nanoneedle on top of it. For the deposition of the nanoneedle system, 1:25 ratio of zinc nitrate and sodium hydroxide was dissolved in 50 ml of deionized distilled water in a glass beaker and stirred continuously at 300 rpm, at a constant bath temperature of 343K. The required pH balance of the solution is very crucial for the deposition of ZnO nanoneedle system and hence the pH was monitored and the pH balance of the aqueous medium was maintained by adding more deionized distilled water, if the pH changed due to evaporation. The ZnO buffer layer coated ITO glass substrate and quartz substrates were dipped into the solution from above the beaker attached to a custom made Teflon beaker stopper. The stopper also had provision for attaching a thermometer for monitoring the solution temperature at all the time. The total deposition process was carried out for 3h after which, the substrates were removed, washed by trickling deionized and distilled water slowly from the backside of the substrate and then dried at 423K in open air. This process yield clusters of ZnO nanoneedles on top of the substrate. Thus deposited ZnO nanoneedle cluster thin films were characterized microstructurally by SEM and XRD. The optical characteristic of the film was studied by measuring its transmittance spectra in the wavelength range of λ =350-800 nm (at room temperature) using an UV-VIS-NIR spectrophotometer. The PL spectrum of the ZnO nanoneedle cluster thin film was obtained using a dual channel lock-in amplifier. The illumination source was the 325 nm line of a continuous HeCd laser passed through a chopper spinning at preset frequency of 15 Hz. The sample was mounted on a holder, fitted to a photomultiplier tube and connected to a Stanford Research SR830 dual cannel lockin amplifier to record the variation of luminescence emitted from the sample in the wavelength scanning range of 300 nm to 800 nm. The whole system was interfaced to a computer for automatic data acquisition.

3. RESULTS AND DISCUSSION

Figure 1 shows the SEM micrograph of the ZnO nanoneedle clusters deposited onto ZnO buffer layer coated ITO glass substrate. It can be observed that the nanoneedle clusters are evenly distributed on the substrate. Some secondary overgrowth could be observed along with the nanoneedle cluster. A closer look indicates that each cluster have about 4-10 nanoneedles oriented in various angles about a vertical axis. The needles were tapered at the end. As estimated from the SEM micrograph, the needles had a length of about 1000-1500 nm whereas; the diameter of the nanoneedles was about 100-200 nm. The XRD of an as-deposited ZnO nanoneedle cluster thin film on quartz substrate (not shown here) displayed a strong peak at $2\theta = 34.4$ degrees corresponding to the diffraction from (002) planes of the hexagonal-ZnO (h-ZnO) with wurtzite structure, while other low intensity small peaks for (100), (101) and (103) planes of h-ZnO were also observed at $2\theta = 31.8$, 36.3 and 56.6 degrees respectively (JCPDS card no 36-1451). Thus the ZnO nanostructures had a strong c-axis oriented growth, which was the main reason behind the formation of the 1d nanostructures. The optical transmittance spectrum of a representative ZnO nanoneedle cluster thin film deposited on quartz substrate is shown in figure 2.
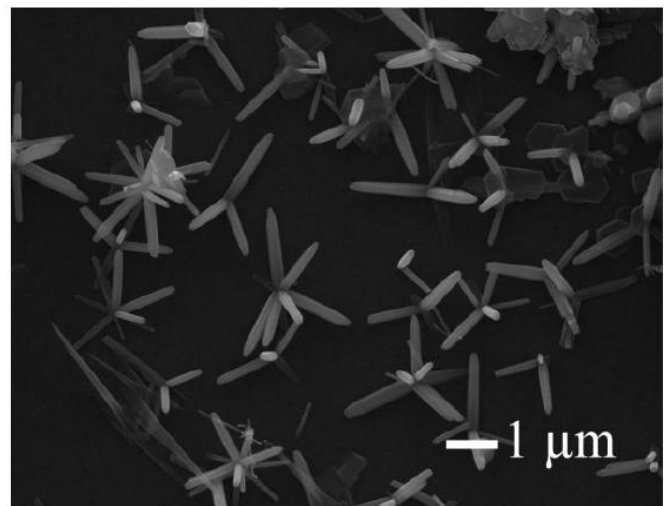
Fig. 1: ZnO nanoneedle clustered thin film

From the Figure 2, it is evident that the transmittance was greater than 60% in the 450-800 nm wavelength range. Now, the optical absorption coefficient (α) [11] can be calculated from the transmittance plot using the Beer's law. Then, $\alpha(\lambda) = \ln(1/T)/d$, where d is the film thickness. Again, the optical absorption coefficient (α)

can be related with the photon energy hν and band gap E_g as, $\alpha h\nu = A (h\nu - E_g)^{1/m}$, where A = constant and m= ½ or 2 depending on whether the optical transition within the material is indirect or direct type. Since direct transition occurs in ZnO, therefore, plotting the $(\alpha h\nu)^2$ versus hν plot and extrapolating to α =0, the bandgap is obtained. In our case, the bandgap obtained was about 3.21 eV for the ZnO nanoneedle cluster thin film deposited on quartz substrate. The PL of the ZnO nanoneedle cluster thin film deposited on quartz substrate was performed at room temperature (300K) using the 325 nm line of a HeCd continuous laser. The PL spectrum demonstrated a broad yellow-orange luminescence peak centered around 2.1 eV corresponding to the transition from the Zn interstitial to the oxygen interstitial, and thus can be attributed to oxygen related defects on the nanoneedle surface [12]. No band edge luminescence was observed at room temperature.
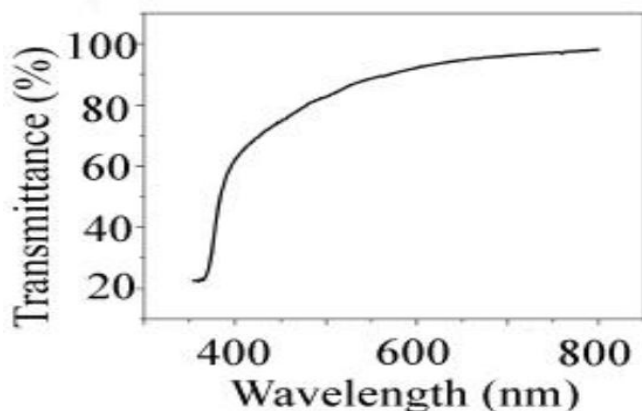
Fig. 2: Optical transmittance of the ZnO nanoneedle thin film

4. CONCLUSION

ZnO nanoneedle cluster thin film was deposited onto quartz and ITO coated glass substrates by a facile, low cost solution deposition process with low thermal budget. The typical nanoneedles were 1000-1500 nm in length and 100-200 nm in diameter and had a tapered end. The nanoneedle clusters were uniformly distributed onto the ZnO buffer layer coated quartz and ITO glass substrate. The XRD of the samples indicated a large peak corresponding to diffraction from (002) planes of h-ZnO with wurtzite structure along with smaller peaks at (100), (101) and (103), also for h-ZnO.

The large (002) peak confirmed the c-axis oriented growth of the ZnO nanostructures. This was mainly responsible for the unidirectional growth of the nanostructures and helped in the formation of the 1d structure. The films showed appreciable transparency in the visible wavelength range of 400-800 nm, as was confirmed by the transmittance trace. A direct bandgap of 3.21 eV was obtained for the ZnO sample. The PL spectrum demonstrated a broad yellow-orange luminescence peak centered around 2.1 eV, which can be attributed to oxygen related defects on the nanoneedle surface.

5. ACNOWLEDGEMENT

6. REFERENCES

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