



ZnO film deposition by RF-magnetron sputtering: UV-Visible absorption and photoluminescence studies

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Abstract:

ZnO films were deposited for different time durations on glass substrates by rf magnetron sputtering. Thickness of the deposited films were determined from the transmission spectra taken using UV-Visible absorption spectrometer. Increase in the thickness of the film with time of deposition showed a linear behavior. Further UV-Visible absorption studies were carried out to look at the band-edge transition and corresponding band-gap energy determination using Tauc plot. XRD analysis and AFM topography of deposited ZnO films showed preferred oriented growth in (002) plane. The XRD and Raman analysis show the crystalline nature of the films deposited. A narrow and broad PL emission additionally confirms the purity and presence of minimal defects in the deposited film.

Keywords: rf-sputtering, ZnO films, Oriented growth, Raman spectrum

Introduction:

Zinc oxide which is one of the most versatile and promising materials for its applications in photo diodes, UV lasers, gas sensors and solar cells which has been a target material for many research groups [1, 2]. ZnO with a wide band-gap of ~3.2-3.4 eV and a large exciton binding energy of 60 meV is a potential candidate for the mentioned applications. Efforts have been focused on mainly preparing nanostructures and thin films. It is well established in literature that the properties of the film strongly depend on the deposition method as well as the parameter used during deposition. Especially the degree of crystallization in ZnO films has a strong influence on the emission efficiency and device performance [3]. ZnO thin films may be prepared using different chemical, electrochemical and physical methods. The films prepared by physical techniques are more uniform, stable and strong as compared to the films prepared by the other two techniques. ZnO thin films have been prepared using different physical techniques such as molecular beam epitaxy [4, 5], RF magnetron sputtering [6], pulsed laser deposition [7, 8] and electron beam evaporation [9]. RF-magnetron sputtering is opted for a large range of industrially important coatings and offers the same functionality as much thicker

films using other coating techniques. Moreover, this deposition technique makes a significant impact in application areas like corrosion resistant coatings, low friction coatings, hard and wear resistant coatings, decorative coatings and coating with specific optical and electrical properties [10, 11]. Oxygen defect induced strong green emission has been reported in various PL investigations [12-15]. So, it has instilled in us to investigate the defect induced green emission in these highly stable and pure rf sputtered ZnO thin films.

In this research paper, it's reported the deposition of ZnO films by RF-magnetron sputtering technique with a preferred oriented growth. The thickness of the deposited films was determined using transmission studies. Further band-gap determination was carried out using UV-Visible absorption studies using Tauc plot. XRD, Raman and AFM analyses were carried out to study the crystallinity and surface morphology of the films deposited. Photoluminescence studies were mainly carried out to investigate purity and presence of defects in the sample under investigation.

Experimental details:

RF – magnetron Sputtering unit with radio frequency of 13.56 MHz from Hind-hivac Vacuum System was used for the deposition of the films. A ZnO target (99.99% pure) of 2-inch diameter and 2 mm thickness was used for the said deposition. The deposition conditions were optimized for 216 Watts power and 0.04 mbar Ar pressure for our system and for the ZnO film deposition. (15×25) mm glass pieces cut from BK7 micro-slides were used as substrates for depositing the films. ZnO films were deposited for different time durations (viz. 15, 22 and 30 minutes) to standardize the film thickness with time of deposition. After optimization, 500 nm thick ZnO films were deposited. And further characterization and other studies were carried out for the deposited samples.

The structural characterization was done using X-ray diffraction measurements using Rigaku RU-200 with Cu K α line of 1.54056Å. Surface morphology of the deposited films was characterized using AFM analysis (Veeco SP-2 Pro). UV-Visible absorption spectra were taken using EVOLUTION 300 UV-VIS (Thermo Scientific). Photoluminescence spectra of ZnO films were taken using Fluorolog (HORIBA JOBIN YVON) and a Xenon lamp was used as the excitation source. The Raman spectra of the thin films were recorded using Renishaw Micro-Raman setup.

Results and Discussions:

After optimization ZnO films were deposited with different times of deposition.

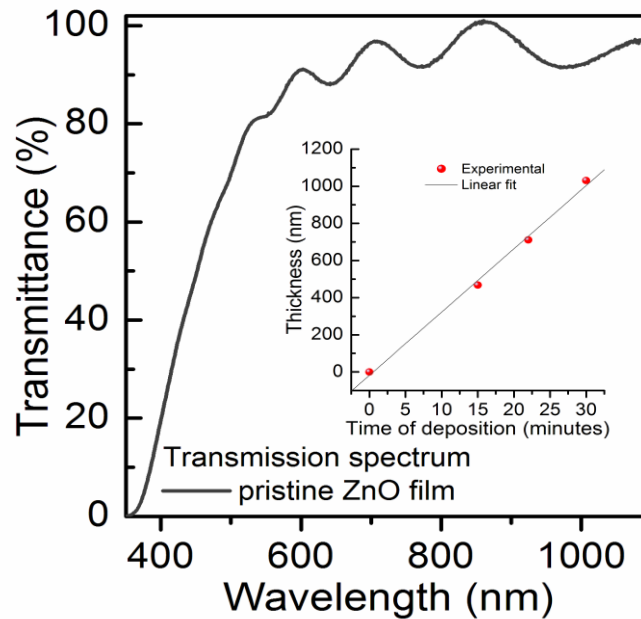


Fig 1. Transmission spectrum of the ZnO film deposited and inset show the film thickness at different deposition time.

Fig 1 shows the transmission spectrum of one of the rf-sputtered ZnO films and inset shows the variation of thickness with time of deposition. Transmission spectra of ZnO films deposited for different time durations were used for calculating the thickness of the films using the following relation:

$$t(\text{nm}) = \frac{N\lambda_1\lambda_2}{2[\eta(\lambda_1)\lambda_2 - \eta(\lambda_2)\lambda_1]} \quad (1)$$

Where t - thickness of the film, N - number of oscillations between the two extrema ($N=1$ for two consecutive maxima or minima). $\lambda_1, \eta(\lambda_1)$ and $\lambda_2, \eta(\lambda_2)$ are corresponding wavelengths and indices of refraction respectively [16]. Calculated thickness of the film plotted against the time of deposition shows a linear behavior which is shown in the inset **Fig 1**. Accordingly, the time of deposition was fixed for 15 minutes for all the subsequent deposition of ZnO films so as to deposit round 500 nm thick films.

X-ray diffraction (XRD) studies were carried out for the deposited ZnO films using a Cu-K α radiation ($\lambda = 1.54056 \text{ \AA}$) in the range $20^\circ - 80^\circ$. **Fig 2** shows the XRD pattern of one of the deposited ZnO films. Peaks were observed at two theta degrees of $31.83^\circ, 34.52^\circ, 36.32^\circ, 47.57^\circ, 56.56^\circ, 62.84^\circ, 68.00^\circ$ which have been indexed to the planes of values (100), (002), (101), (102), (110), (103) and (112) for ZnO which matches with the JCPDS card no. 36 – 1451. (002) plane preferred oriented growth is observed from the XRD spectra showing highest intensity peak.

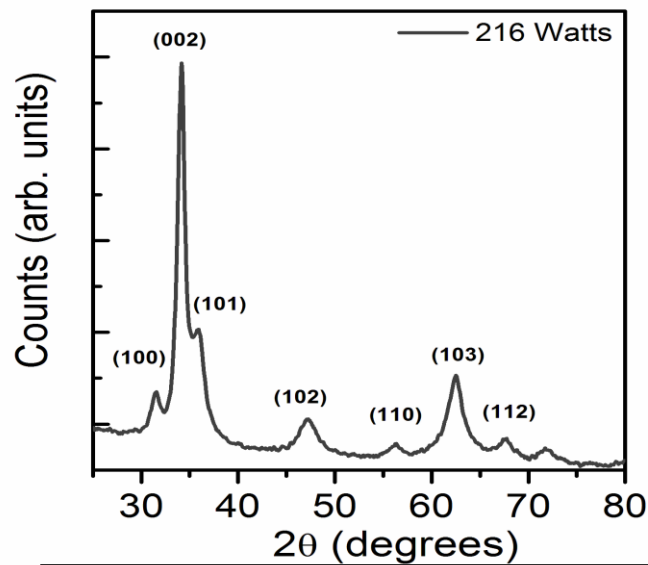


Fig 2 XRD spectra of the rf sputtered ZnO film

It indicates that the nanostructures of the film seem to be rod like/ pillar like. To investigate further, AFM analysis was carried out.

Fig 3(a) shows 3D AFM micrograph of $5\mu\text{m} \times 5\mu\text{m}$ area of the deposited film and Fig3(b) shows AFM micrograph of $1\mu\text{m} \times 1\mu\text{m}$ area, an enlarge image. AFM analysis of the ZnO films deposited also show preferred Z-direction oriented growth supporting the XRD analysis. It also shows a good uniformity in the deposited films.

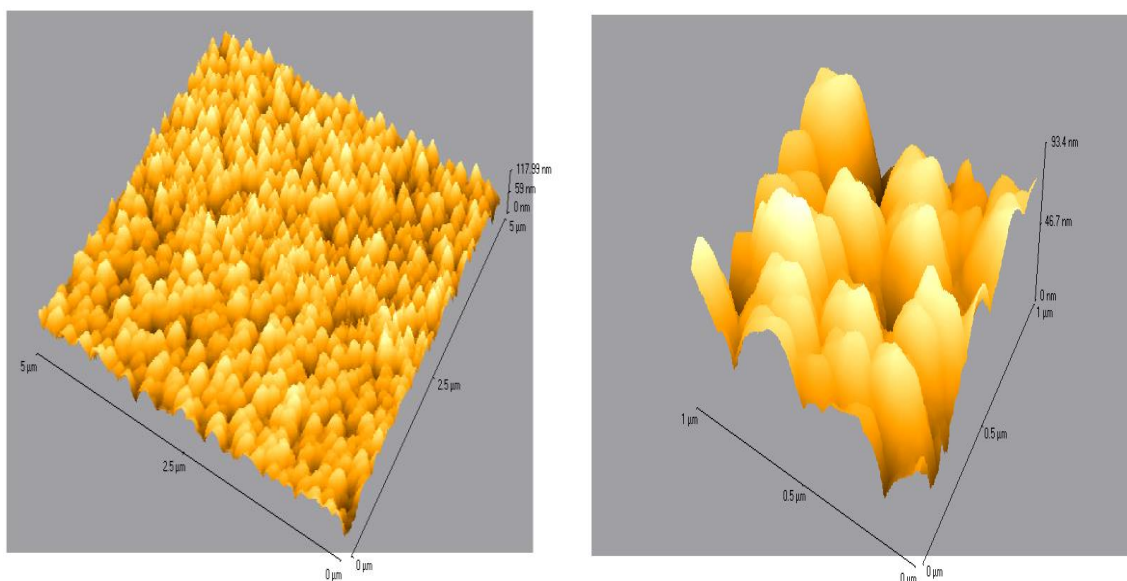


Fig 3 AFM analysis of ZnO film (a) $5\mu\text{m} \times 5\mu\text{m}$ film area & (b) an enlarged version

The structure and crystallinity of the ZnO films was further confirmed from the Raman studies. ZnO belongs to the hexagonal wurtzite structure with each zinc ion surrounded tetrahedrally by four oxygen ions and *vice versa*. At Brillouin zone G point, group theory predicted of the optical phonon modes $A_1 + 2B_1 + E_1 + 2E_2$. A_1 , E_1 , and E_2 are modes which are Raman active and the B_1 mode is forbidden [17, 18]. The assignment of the various Raman peaks has been well established in literature [19-21].

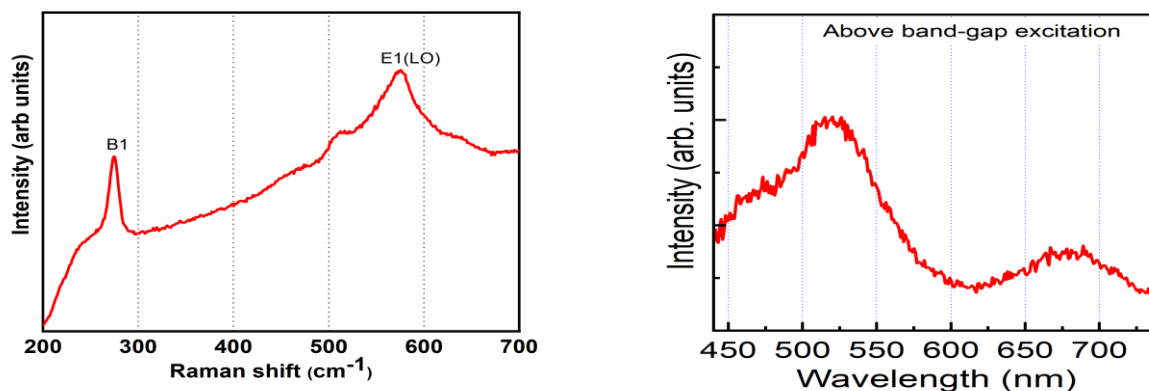


Fig 4(a) Raman spectra of the deposited ZnO film. (b) PL spectra of the deposited ZnO

Off-resonance Raman spectrum of the deposited film is shown in fig 4(a). The Raman peaks are clearly observed at 275 cm⁻¹ and 576 cm⁻¹. The peak at 275 cm⁻¹ is attributed to $B_1(\text{low})$ which are generally forbidden. Appearance of $B_1(\text{low})$ mode can be mainly attributed to the ZnO nanorods in which the geometric boundaries and high surface-to-volume ratios disrupt long-range lattice periodicity and termed disorder activated Raman scattering. Activation of $B_1(\text{low})$ mode indeed supports our XRD and AFM analyses showing preferred oriented growth of the nanocrystals in the z-direction.

The broad peak at 576 cm⁻¹ is assigned to the $E_1(\text{LO})$ mode in agreement with the reported for bulk, thin film and nanocrystals [20, 22-28]. The shift in the peak position may be attributed to the crystal disruption and oxygen vacancies produced due to the preparation technique.

We know that ZnO nanostructured films exhibit PL emission in the visible region at different wavelengths due to the intrinsic defects present. In the PL spectra, a broad emission in the green region centered around 520 nm is observed. Fig 4(b) shows the PL spectra of the deposited film. It is quite clear that green emission exhibited by ZnO nanostructures is due to presence of oxygen defects. The origin of green emission has been credited to different reasons. Vanheusden et al [29] has attributed it to transition between singly ionized oxygen vacancy and photoexcited hole. Dijken et al [30] proposed the green emission to be due to the transition between electrons close to the conduction

band and a deeply trapped hole at V_0^{++} and Djuriscic et al [31] proposed the cause as surface defects. And a narrow broad red emission in the PL spectra centering around 680 nm may be attributed to the intrinsic point defects within the crystal. These defects introduce specific deep-level acceptor or donor states within the band-gap.

UV-Visible absorption spectrum of ZnO film show band-edge transition clearly which is shown in **Fig 5**. This spectrum was used to calculate the band-gap of the deposited ZnO films using Tauc plot. Inset shows the corresponding band-gap calculated and is found to be 3.403 eV. The larger band-gap energy as compared to the bulk reveals the very fine nature of the clusters constituting the ZnO film.

Conclusions:

Thin films of ZnO were deposited on glass substrates by rf-magnetron sputtering. 15 minutes deposited films were found to be around 500 nm thick which was determined from the linear curve plotted for different time depositions of ZnO. Raman and XRD analyses confirm the good crystalline nature of the deposited films. Moreover, the nanostructures of the films show preferred oriented growth along the z-direction. The ZnO films deposited using this particular method of method was found to be around 3.4 eV. The high value of the band-gap may be attributed to the fine nature of the nanostructures constituting the film.

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