Effect of substrate on physical properties of pulse laser deposited ZnO thin films

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ZnO is a II-VI group semiconductor material with a large direct band gap. Zinc oxide films are prepared by Pulse Laser Deposition (PLD) technique on to highly cleaned glass, ITO coated glass and Si (100) substrates. The as-prepared films are characterized by optical absorption and transmission spectra and X-Ray Diffraction (XRD) patterns. The absorption spectra and transmission spectra of the deposited ZnO films are taken from UV-VIS-NIR Spectrophotometer at room temperature. The band gap of the ZnO film is determined from absorption measurements using Tauc relation for direct band gap materials while optical constants of the ZnO film are determined from transmission measurements by Manifacier’s envelope method. The effect of lattice mismatching between the lattices of the substrate and of the deposited material on the structural properties and crystallite size of the deposited films are studied using XRD patterns of ZnO films.

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1. Introduction

ZnO is an immensely popular II-IV semiconductor material with wide and direct band gap (3.37 eV) and large exciton binding energy1 (60 MeV). It is not quite possible to enumerate all applications for ZnO, but many promising uses are related to its semiconductor properties and its transparency to visible light. It is an attractive and promising material for many applications such as surface acoustic wave devices (SAW)2, light emitting diodes3, laser diodes5, photo detectors5, Solar cell windows2 and gas sensor2. Recently, highly resistive and c-axis oriented polycrystalline ZnO thin films have been grown on Ti/SiO2/Si substrates by RF magnetron sputtering technique for nonvolatile resistance memory switching applications. It is scarcely possible to list all research work done by various researchers on ZnO thin films. Various growth techniques such as chemical vapor deposition7, r.f. magnetron sputtering10-12, pulsed laser deposition (PLD)13-15, evaporation16, spray pyrolysis17, photo-atomic layer deposition18, metal oxide chemical vapor deposition (MOCVD)19, molecular beam epitaxy (MBE)20 and sol-gel process21,22 have been used for deposition of ZnO films.

The properties of semiconducting films though primarily determined by the material of the film; however their physical properties are greatly affected by the technique of film deposition, and also the compatibility with the lattice parameters of the substrate. The material and orientation of the substrate material have characteristic effect on the nucleation and growth dominated microstructure of a thin film and there by on its physical properties. Deposition of single crystalline, polycrystalline of amorphous thin films depends on the growth conditions and the substrate. While depositing the film the mismatch between the lattices of the substrate and of the deposited material play a vital role on the properties of the deposited film, especially near the contact interface. For thick films the lattice mismatch tapers out and the material exhibit the bulk properties although crystallinity of the deposited film may not be good. For very thin films the properties would be essentially dominated by the lattice mismatch at the interface.

The challenge associated with growing oxides is to provide and control the amount of oxygen during the growth to obtain the desired oxygen stoichiometry and hence appropriate physical properties of the respective oxide. For a depositing pulsed laser deposition (PLD) is often seems to be sufficient to create the correct amount of plasma species with in an oxygen background to form the chosen compound as a thin film on a suitable substrate and to supply the missing oxygen with a subsequent annealing step. During a deposition, the only discussed and usually considered oxygen sources are the target and the background gas. The substrate taken as template for the film preparation to be match the respective lattice constants to grow oxide film e.g. epitaxially, with a preferred crystalline orientation22. In this paper, we report the synthesis of ZnO thin films by pulsed laser deposition technique on glass, ITO coated glass and Si substrates and reported the structural and optical properties of as-deposited films. The effect of lattice mismatching between the lattices of the substrate and of the deposited material on the structural properties of the deposited film also discussed in detail.

2. Experimental

Zinc Oxide films have been prepared by pulsed laser deposition (PLD) technique onto highly cleaned glass, ITO Coated glass and Si Substrates. The target of ZnO was prepared using 99.99% pure ZnO Powder. This powder
was grinded for 6 hr and then calcined at 450 °C for 10 hr. The calcined powder was regrinding for 8 hr and was then pressed into pellets of 15 mm in diameter and 2 mm thickness under the pressure of 60 MPa. Then, the pallets were sintered at 800°C. The Si substrates were cleaned sequentially with diluted HF solution, distilled water and acetone. Glass and ITO coated glass substrate was cleaned with distilled water and acetone. ZnO thin films have been deposited on different substrate using pulsed laser deposition (PLD) technique employing a KrF laser source ($\lambda$=248 nm). Various parameters used in pulsed laser deposition technique are shown in Table 1. We rotated the target at 2 rpm to avoid texturing of the target surface. The thickness of the grown film is typically ~250 nm and buffer layer thickness is ~50 nm.

### Table 1: Various parameters used in deposition of ZnO crystalline thin films by pulsed laser deposition technique.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser source</td>
<td>KrF eximer source</td>
</tr>
<tr>
<td>Laser wavelength</td>
<td>248 nm</td>
</tr>
<tr>
<td>Laser energy</td>
<td>300 mJ</td>
</tr>
<tr>
<td>Laser fluence</td>
<td>2-3 J-cm$^{-2}$</td>
</tr>
<tr>
<td>Repetition rate</td>
<td>10 Hz</td>
</tr>
<tr>
<td>Target used</td>
<td>ZnO,</td>
</tr>
<tr>
<td>Base pressure</td>
<td>$2 \times 10^{6}$ Torr</td>
</tr>
<tr>
<td>Gas used (99.7%)</td>
<td>High purity oxygen</td>
</tr>
<tr>
<td>Deposition pressure</td>
<td>50 m Torr</td>
</tr>
<tr>
<td>Substrates used</td>
<td>Si (100), glass, ITO coated glass</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>500 °C</td>
</tr>
<tr>
<td>Target to substrate distance</td>
<td>30 mm</td>
</tr>
</tbody>
</table>

The phase and orientation of as-grown thin films were characterized by X-ray diffractometry using CuK$_\alpha$ ($\lambda$=1.5407 Å) radiation. The surface topography and microstructure were examined by atomic force microscope (AFM). The Optical transmission and absorption spectra are used to study the optical properties of deposited films and have been taken using UV-VIS-NIR spectrophotometer in the wavelength range 300 to 1200 nm.

### 3. Results and discussion

#### 3.1. XRD Diffraction

Figure 1 shows the XRD pattern for the deposited ZnO films on: (a) glass substrate (b) ITO coated glass substrate and (c) Si substrate. The Diffraction peak appeared in the XRD pattern can be indexed as (002) peak of the as grown ZnO films indicating that the films were highly preferred c-axis orientation. In addition to this, ITO and Si peak also emerged in the pattern of ZnO film deposited on ITO coated glass and Si substrate respectively.

It is seen that lattice mismatch between the substrate and the deposited material plays a vital role on the properties of the deposited film, especially near the contact interface. For very thin films the properties would be essentially dominated by the lattice mismatch at the interface. This can be seen from the XRD’s of ZnO films deposited on glass, ITO coated glass and Si substrates respectively as shown in the Figure 2. In case of glass the concept of lattice parameters as envisaged from the crystallinity point of view for crystalline substrates is almost missing, therefore the deposited film would have its lattice parameters grossly distorted because of the lattice mismatch and its properties would deviate appreciably from the bulk properties of ZnO. For ITO coated glass the crystallinity of tin oxide though not perfect, is still better than that of uncoated glass therefore the vapours getting deposited on the ITO coated substrate would find a better lattice for getting deposited and hence the lattice mismatch will be not only will be lesser but would extended upto a lesser thickness of the film. When a good crystalline substrate like Si is used for depositing the film than lattice matching with the deposited film material would be better and more uniform laterally along the surface and such a film exhibit properties which would be nearest to the bulk properties of the deposited material.
This phenomena is aptly demonstrated in the Figure 2, where the XRD patterns relating to the (002) peaks for ZnO which for a good crystalline specimen would appear at an angle of 34.4° is found to occur at 34.75° for glass substrate, 34.66° for ITO, and 34.59° for Si substrate i.e the peak is shifting towards its value for the bulk substrate as crystallinity of the substrate increases. Hence, the XRD peak approaches more and more towards its value for the bulk ZnO material, as the crystallinity of the substrates increases from pure glass, ITO coated glass to crystalline silicon.

The crystal size ‘t’ of the as grown films was determined by using the Debye Scherrer formula

\[ t = \frac{0.9 \lambda}{B \cos \theta} \]

Where \( \lambda \) is the X-ray Wavelength (1.54 Å), \( \theta \) is the Bragg diffraction angle, and B is the FWHM of the (002) peak, respectively. The crystallite size of the as grown films on Glass, ITO coated Glass and Si Substrate was found to be 45.89nm, 38.11 nm and 36.28 nm respectively.

3.2. Optical Characterization

Optical properties of ZnO thin films deposited on glass & ITO coated glass substrate were studied with the help of absorption and Transmission Spectra taken at room temperature.

Determination of energy band gap (\( E_g \)):

The absorption spectrum of the material is an important technique which is used for measuring the energy band gap of a semiconductor. An important feature of this method is that it is applicable for any range that is narrow or wide band gap material. In this experiment photons of selected wavelength are incident on the sample and the relative transmission of the various photons is observed.

To determine the energy gap from absorption spectra (shown in Fig. 3) the Tauc relation for direct transition is used[24]. A plot of \( (a \nu)^2 \) versus photon energy \( (\hbar \nu) \) when extrapolated to zero absorption gives the value of energy band gap\( (E_g) \) as shown in Fig. 4. The band gap of ZnO thin films deposited on glass and ITO coated glass substrates comes out 3.27eV and 3.38 eV respectively.

Determination of Optical Constants:

The Optical transmission spectra of as deposited ZnO thin films on glass and ITO glass substrates was recorded in the wavelength range 300-900 nm are shown in Fig. 5.
These are interference fringes due to multiple reflections of light taking place between the lower surface in contact with the substrate and the free surface of the film. Figures 5 shows the optical transmission spectrum of ZnO crystalline thin film deposited on glass substrate and ITO coated glass substrate. This spectrum can be divided mainly into three regions: The transparent region (450 -1000 nm): the absorption coefficient is very close to zero; the transmission is determined by both refractive index of film and the refractive index substrate material through multiple reflections. The region of weak absorption (380-450 nm), in this wavelength region α is small but begins to reduce transmission towards lower wavelength. The region of strong absorption (below 380 nm), in this wavelength region drastic decrease of the transmission is caused by the film absorption due to the transition between the valence band and conduction band.

The optical constants (Refractive index n and the extinction Coefficient k) of ZnO films on glass and ITO glass substrates were calculated from transmittance measurement by using Manifacier’s envelop method\textsuperscript{25}, where the refractive index ‘n(λ)’ at any wavelength λ is given by

\[
n(λ) = \left[ N + \left( N^2 - n_0^2 n_1^2 \right)^{1/2} \right]^{1/2}
\]

where \( N = \frac{(n_0^2 + n_1^2)}{2} + 2n_0 n_1 \left( \frac{T_{max} - T_{min}}{T_{max} - T_{min}} \right) \),

\( T_{max} \) & \( T_{min} \) being the values of film transparencies as represented by the envelope of the extremas in the percentage transmission curves shown Fig. 5, \( n_0 \) and \( n_1 \) being the refractive indices of air and the glass substrate & ITO coated glass respectively. From the different values of \( N \) and ‘n(λ)’ at different wave lengths, the thickness ‘t’ of the film was determined by the relation\textsuperscript{24}.

\[
t = \frac{(M \lambda_1 \lambda_2)}{2} \left[ n(\lambda_1) \lambda_2 - n(\lambda_2) \lambda_1 \right]
\]

where M is the number of oscillations between two extrema corresponding to wavelength \( \lambda_1 \) and \( \lambda_2 \) in the transmission curve.

From the value of ‘t’, the extinction coefficient ‘k’ can be calculated from

\[
k = \frac{-\lambda}{4\pi t} \ln P
\]

where \( P = \frac{(n+n_0)(n_1+n)(1- \left( \frac{T_{max}}{T_{min}} \right)^{1/2})}{(n-n_0)(n_1-n)(1+ \left( \frac{T_{max}}{T_{min}} \right)^{1/2})} \)

Fig. 6 and 7 shows the variation of optical constant (n, and k) with wavelength (λ) for ZnO thin films deposited on glass and ITO coated glass substrates. From the figure 6 and 7, it is clear that refractive index (n) decreased with increasing wavelength (λ) of ZnO crystalline thin films deposited on glass and ITO coated glass substrates respectively. These results are in conformity with the results calculated from Sellmeir’s equation\textsuperscript{26}. As we move away from the absorption edge towards the longer wavelength, transitions involving donor level, acceptor level and traps and even intraband transitions would become more pronounced\textsuperscript{27}. These would results in more losses, which are reflected in the increased k with the increasing wavelength. The decreased absorption will also reflected in lower value of n as is also evident from the mathematical expressions for n and k as given in this section.
4. Conclusions

The above evaluation of ZnO thin films grown on Glass, ITO Coated Glass and Si(100) substrates lead to the important inference that apart from other factors, the compatibility of lattices of the film material and the substrate interface vitally decide the structural characteristics and the physical properties of the film. Obviously this would be a very important criterion in the design of thin film devices and their operational life.

References


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