Study of Optical Characterization of Pulse Laser Deposited ZnO Thin Films

Shweta Vishnoi¹ Rakesh Kumar² Sunder Pal³ Beer Pal Singh⁴

Abstract

ZnO is a II-VI group semiconductor material with a large direct band. Zinc oxide film has been prepared by pulsed laser deposition (PLD) technique on to highly cleaned glass substrate. The as-prepared film is characterized by optical absorption spectra and transmission spectra, X-Ray Diffraction (XRD) pattern and Atomic Force Microscopy (AFM). The absorption spectra and transmission spectra of the ZnO film have been taken from UV-VIS-NIR Spectrophotometer at room temperature. The absorption spectra are used to calculate the band gap of the ZnO film by Tauc’s relation for direct band gap material only. The transmission spectra are used to calculate the optical constants of the ZnO film by Manifacier’s envelop method. The X-ray diffraction pattern of ZnO is used to calculate crystallite size by Scherrer formula.

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Introduction

ZnO is the II-IV semiconductor material with wide and direct band gap (3.37 eV) and large exciton binding energy (60 MeV) [1]. It is an attractive and promising material for many applications such as surface acoustic wave devices (SAW) [2], light emitting diodes [3, laser diodes [4], photo detectors [5], solar cell windows [6] and gas sensors [7]. Various growth techniques such as chemical vapor deposition [8], r.f. magnetron sputtering [9], pulsed laser deposition (PLD) [10], evaporation [11], spray pyrolysis [12], photo-atomic layer deposition [13], metal oxide chemical vapor deposition (MOCVD) [14], molecular beam epitaxy (MBE) [15] and sol-gel process [16] have been used for ZnO film.

Currently, many research groups are working on this material. Amit Kumar et al. [17] have deposited ZnO thin films by a RF magnetron sputtering technique and studied their nonvolatile resistance memory switching properties. Amit Kumar et.al [18] have synthesized Al-N coded ZnO thin films deposited on n-Si substrate by RF magnetron sputtering technique and shown the induction of p-type conduction in deposited Al-N coded ZnO thin film. Amit Kumar et.al [19] have fabricated p-type ZnO epitaxial thin films and studied their physical properties. Jean Paul
Mosnier et al. [20] have deposited ZnO films by Pulse Laser Deposition on soda lime glass substrate for the ultraviolet inactivation of Staphylococcus epidermidis bio-films. Schristoulakis et al. [21] have prepared ZnO nanostructures transparent thin films of different thickness on silicon and coning glass substrate by pulse laser deposition and show that sensing properties can be controlled by modifying the deposition condition.

2. Experimental

Zinc oxide films have been prepared by pulsed laser deposition (PLD) technique onto highly cleaned glass substrates. The target of ZnO was prepared using 99.99% pure ZnO powder. This powder was ground for 6 hours and then calcined at 450 °C for 10 hr. The calcined powder was reground for 8 hours and was then pressed into pellets of 15 mm in diameter and 2 mm thickness under a pressure of 60 MPa. Then, the pallets were sintered at 800 °C . Glass was cleaned with distilled water and acetone. ZnO thin film has been deposited on glass substrate using pulsed laser deposition (PLD) technique employing a KrF laser source (λ=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>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser source</td>
<td>KrF eximer source</td>
</tr>
<tr>
<td>Laser wave length</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 × 10-6 Torr</td>
</tr>
<tr>
<td>Gas used</td>
<td>High purity oxygen (99.7%)</td>
</tr>
<tr>
<td>Deposition pressure</td>
<td>50 m Torr</td>
</tr>
<tr>
<td>Substrate used</td>
<td>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 film was characterized by X-ray diffractometry using CuKα (λ=1.5407 Å) radiation. The surface topography and microstructure were examined by an atomic force microscope (AFM). The optical transmission and absorption spectra have been taken using UV-VIS-NIR spectrophotometer in the wavelength range 300 to 1400 nm.

3. Results and discussions

XRD Deraction

Figure 1 shows the XRD pattern as grown ZnO thin film on glass. The Diffraction Peak appeared in the XRD Spectra can be indexed as (002) peak of the as grown ZnO film. The crystallite size "t" of the as grown films was determined by using the Scherrer formula [22].

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

Where λ is the X-ray wavelength (1.54 Å), θB is the Bragg diffraction angle and B is the FWHM of the (002) peak, respectively. The crystallized size of the as grown film of ZnO was found to be 45.89nm.

Optical characterization

Optical properties of ZnO thin film was studied with the help of absorption and Transmission Spectra.

Determination of energy band gap

(Eg): 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 wave length are incident on the sample and the relative transmission of the various photons is observed.

To determine the energy band gap from absorption spectra, the Tauc relation is used [16].

\[ a h v = A (h v - E_g)^n \]  

where, \( h v \) = Photon energy  
\( E_g \) = Band gap  
\( a \) = Absorption coefficient  
\( A \) = Constant  
\( n \) = \( \frac{1}{2} \), allowed direct transition

A graph was plotted between \((a h v)^2\) and \(h v\) (as abscissa), a straight line was obtained. The extrapolation of a straight line to \((h v)^2 = 0\) axis gives the value of the band gap to film material.

Fig. (2) represents the absorption spectra of ZnO film in the wave length range 300-800 nm. In fig. (3) we have plotted a graph between \((a h v)^2\) and \(h v\), for the determination of optical band gap. The band gap of ZnO film comes out 3.26 eV

\[ \text{Figure 2: Absorption spectra of ZnO thin film} \]

\[ \text{Figure 3: Determination of energy band gap of ZnO thin film.} \]

**DETERMINATION OF OPTICAL CONSTANTS**

The optical transmittance spectra of as deposited ZnO film in the wave length range 300-1400 nm are shown in fig. 4.

The optical constants (Refractive index \(n\) and the extinction coefficient \(k\)) of ZnO film have been determined from transmittance measurement by using Manifacier’s envelop method [23].

The refractive index \(n\) and extinction coefficient \(k\) were calculated using the formula [23]

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

Where \(n_0\) is the refractive index of air; \(n_1\) is the refractive index of substrate and the number \(N\) is given by

\[ N = n_0^2 + n_1^2 + \frac{2 n_0 n_1 (T_{\text{max}} - T_{\text{min}})}{T_{\text{max}} T_{\text{min}}} \]

Where \(T_{\text{max}}\) is the upper extreme transmission point and \(T_{\text{min}}\) is the lower extreme transmission point of a particular wave length.

The extinction coefficient \(k\) is given by

\[ k = \left( -\frac{1}{4\pi t} \right) \ln P \]

where \(t\) is the thickness of the film and calculated by the formula

\[ t = \frac{M \lambda_1 \lambda_2}{2 \left[ n_1 (\lambda_1) - n_2 (\lambda_2) \right]} \]

Where \(M\) = no. of two consecutive max or min and

\[ P = \frac{(n + n_0)(n_1 + n)}{(n - n_0)(n_1 - n)} \times \frac{(1 - T_{\text{max}}/T_{\text{min}})}{(1 + T_{\text{max}}/T_{\text{min}})} \]

Table 2 shows the variation of optical constant...
(n, and k) with wave length for ZnO thin film.

Table 2

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Energy (eV)</th>
<th>T\text{max} (%)</th>
<th>T\text{min} (%)</th>
<th>N</th>
<th>n</th>
<th>k</th>
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<td>1.656</td>
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</table>

Conclusions

ZnO thin films were grown on highly cleaned glass substrate by pulse laser deposition. Absorption and transmission spectra are sufficient to calculate the optical constants of ZnO films. It is an accurate, fast and simple method for the determination of optical constants of semiconducting thin films.

References

17. Amit Kumar, Manoj Kumar and Beer Pal Singh, IJAEST Vol No. 1, Issue No. 2, 118-122
18. Amit Kumar, Manoj Kumar and Beer Pal Singh, Optic Communications 283 (2010) 3994-3997