Structural, optical and morphological studies of SILAR grown ZnO thin film and double coated CBD grown ZnO thin film

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Abstract. The Zinc oxide thin films were produced on glass substrate by using SILAR and CBD methods. The structural, optical and morphological properties of the films were investigated by X-Ray diffractometer, UV-visible spectrometer and scanning electron microscopy respectively. The XRD pattern shows that in both the samples preferential growth orientation is along (0 0 2) plane. The optical band gap was found to be 3.31eV for SILAR ample and 3.18eV for CBD grown sample. The morphology analysis shows that the particle size in SILAR grown sample was high. A vertically aligned nanorods were obtained in CBD grown sample.

1. Introduction
The II-IV group semiconductor material ZnO has got a great attention in the field of material science research over the last decades due to its very good optical and electrical properties. Also it possess high chemical and mechanical stability [1]. ZnO has an n-type conductivity due to interstitial zinc atoms and oxygen vacancies [2]. Other important characteristics of ZnO are, it has wide band gap (3.37 eV), inexpensive, non-toxic and possess high exciton binding energy (60meV) [3]. ZnO has wide range of applications in the field of gas sensors [4], transparent conducting windows in solar cell devices [5-6], opto electronics [7-8], thin film transistors [9], diodes [10], and UV photo detectors [11]. Various methods has been adopted for the synthesis of ZnO thin films, such as, SILAR [12], chemical vapor deposition [13], ultrasonic spray pyrolysis[14], pulsed laser deposition [15], R.F sputtering[16], planar magnetron sputtering [17],chemical bath deposition[18], spray pyrolysis [19], hydrothermal synthesis[20] and electrochemical deposition [21]. Among these methods SILAR and CBD are massively used techniques. These methods are simple, inexpensive and it does not require vacuum and complicated equipment [22].

In this present work ZnO thin films were synthesized on microscopic glass slide through Successive ionic layer adsorption and reaction (SILAR) technique and Chemical bath deposition method. The optical, structural and morphological properties of the prepared films were investigated.

2. Experimental details

2.1. Preparation of ZnO thin films by SILAR technique
All the reagents used were of analytical grade without any further purification. In SILAR method substrate is immersed in the cationic and anionic solutions separately. In this work cationic solution is prepared by using zinc nitrate and aqueous ammonia and hot distilled water is taken as anionic solution. At first 0.25M zinc nitrate solution is prepared by dissolving zinc salt in 120 ml distilled water. The pH
of the solution is adjusted to 9.36 by adding ammonia drop wise to the prepared zinc salt solution. Then the prepared cationic solutions were taken in three separate 40 ml beakers. The anionic solution hot water is taken in three separate 40 ml beakers. Before deposition the glass substrates were cleaned thoroughly with chromic acid followed by distilled water. The cleaned glass substrates were immersed in the cationic solution for 30 s and hot water for 30 s. This process is repeated for 150 cycles at room temperature. At the end of the complete cycle films were rinsed thoroughly with distilled water and dried in air. The dried films were used for characterization.

2.2. Preparation of double coated ZnO thin films by CBD

The double coated ZnO thin films were synthesized via chemical bath deposition technique. Commercial microscopic glass slides were used for the deposition of ZnO thin film. In this process 0.25 M zinc nitrate solution is prepared. After that ammonia solution is added drop wise to the zinc nitrate solution under continuous stirring until the solution become clear and homogeneous. The pH is adjusted to 9.36. Then the cleaned glass slides were placed vertically into the solution without touching the walls of the beaker. Solution is kept on a hot plate at 80°C for one and half hours. At the end of the reaction time, the substrates were cleaned with distilled water and dried. And these ZnO deposited cleaned substrates were again dipped in another 0.25 M zinc nitrate solution and repeated the above process. Finally we obtain double coated ZnO thin films and were used for characterization. The structural characterization studies were done by using Bruker advance X-ray diffractometer with Cu-Kα radiation of wavelength

3. Results and discussions

3.1. Structural studies

The structural studies of prepared films were carried out by using X-ray diffractometer with Cu-Kα radiation of wavelength 1.5405 Å over the diffraction angle 2θ between 20° and 80°. Figure 1 indicates the XRD pattern of SILAR grown ZnO thin film. The films have polycrystalline structure. The diffraction peaks occurs at 23.33, 25.84, 29.29, 32.88, 35.47, 37.43, 38.99, 46.03, 48.54, 57.78, 63.73, 68.9. The most intensive peak occurs at 35.54 which corresponds to (0 0 2) plane. Which indicates the growth of highly c axis oriented film. [23]. In the case of double coated ZnO the most intensive peak occurs at 34.6° correspond to (0 0 2) plane (Figure 2). Other peaks occur at 36.44 and 62.96 but they are very less intensive peaks. In both samples, the peak corresponding to (0 0 2) plane was used to calculate the full width half maxima (FWHM) and crystallite size. The size of the crystallite was calculated by using the relation [24].

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \]  

Where \( \theta \) is the Bragg’s angle, \( \lambda \) is the wavelength of X-rays (1.5406 Å for CuKα), and \( \beta \) is the full width half maximum value of the X-ray diffraction peak.

The dislocation density of the films was calculated by using the equation [25]

\[ \delta = \frac{1}{D^2} \]  

The micro strain was calculated by using the equation [26]

\[ \varepsilon = \frac{\beta \cos \theta}{4} \]
The obtained values of FWHM, crystallite size, dislocation density and micro strain of both the samples for the (0 0 2) plane is given in the table 1.

| Sample Type       | 2θ  (degree) | D value (nm) | FWHM | Dislocation density δ (m⁻²) | Microstrain ε |
|-------------------|--------------|--------------|------|-----------------------------|---------------|
| SILAR grown ZnO   | 35.47        | 6.46         | 1.29 | 0.042x10⁻¹⁵                 | 0.0056        |
| Double coated ZnO | 34.60        | 26           | 0.3199 | 0.676x10⁻¹⁵                 | 0.0013        |

The FWHM value for the SILAR grown sample is high. This broadening in the x-ray diffraction peak shows the systematic decrease in the crystallite size. For SILAR grown ZnO the increase in strain indicates defects are generated in the ZnO lattice. In the case of double coated ZnO the strain value was found to be less. Lower values indicates good crystallization and decreased defect levels [27].

3.2. Optical studies

The optical properties of the synthesized films were studied using Hitachi-U-3410 UV Vis-NIR spectrophotometer in 200 -1000 nm wavelength range. The transmission spectra of SILAR grown and double coated CBD grown ZnO films were shown in Figure 3 and Figure 4 respectively. So many works are carried out in ZnO thin films synthesized via SILAR method. Shei et al [23] synthesized ZnO films by SILAR method at different rinsing temperature in the presence of propylene glycol. They have got 85% to 95% transmission in the visible region. Sreedev et al [28] reported 52% of transmittance to a wavelength of 886 nm in SILAR grown ZnO thin films. In our work we obtained 30% to 50% of transmission in the visible region for SILAR grown ZnO and it is below 30% for the double coated ZnO thin films.
The optical band gap of the as prepared samples were determined by plotting $(\alpha h\nu)^2$ as a function of $h\nu$ and extrapolating the linear portion of graph to $x$ axis using the relation [23]

$$(\alpha h\nu)^2 = A (h\nu - E_g)$$

(4)

Where $A$ is the absorption coefficient, $h\nu$ is the photon energy and $E_g$ is the optical band gap. The optical band gap plot of the SILAR grown and double coated CBD grown films were shown in Figure 5 and Figure 6 respectively.

In the case of SILAR grown ZnO we obtained an optical band gap of 3.31 eV an double coated ZnO it is found to be 3.18 eV. Both these values are nearer to the reported values of ZnO.

3.3. Morphological studies

The surface morphology of the SILAR grown and double coated ZnO thin films were examined by Scanning electron microscope (SEM).
Figure 7 shows the SEM picture of SILAR grown ZnO thin film. It reveals highly uniform and compact structure of the film. It exhibits petal-like morphology. The particle size was measured to be 250 µm. Figure 8 shows the surface morphology of double coated CBD grown ZnO thin film.

The top view of the SEM image clearly reveals that the obtained nanorods were vertically aligned and have a hexagonal shape. The diameter of the ZnO nanorods ranging from 178 nm to 200 nm. This variation may be due to the formation of seed layer in the first coating process. These results are consistent with the XRD data.

4. Conclusion
Zinc oxide thin films were successfully deposited on glass substrate by using successive ionic layer adsorption and reaction (SILAR) and CBD methods. In both methods we obtained a polycrystalline and highly c-axis oriented ZnO thin films. The transmission spectra revealed 30 to 50% of transmittance in
the visible region for SILAR grown ZnO thin film and below 30% transparency for double coated CBD grown film. The optical band gap of SILAR grown sample was found to be 3.31 eV. But in the case of Double coated CBD grown sample a slight decrease in optical band gap was observed (3.18 eV). The SILAR grown sample exhibit a petal like morphology. A vertically aligned nanorods were obtained in the double coated CBD grown samples.

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