Structural, Morphology and Optical studies on ZnO Thin film prepared by sol-gel technique

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Abstract: Zinc oxide thin films were prepared by inexpensive sol-gel spin coating technique. The effects of the rotation per minute (RPM) on structural, morphology and optical properties were studied. The crystal structure was analyzed by X-ray diffraction patterns revealed that all the observed peaks were coincided well with previous data. Average particle size, dislocation density and stress were calculated by using Scherrer formula. The morphologies of the prepared thin films were observed by scanning electron microscope. SEM micrograph of the thin film was changed from agglomerated particles into cordillera like structure as increase RPM. Crystal quality was also investigated by Micro Raman Spectrometer, it showed that the agglomerated particle was good in crystalline form compared to the cordillera like structure of ZnO. Optical properties were studied by photo luminescence spectroscopic technique, the crystallinity of the thin film was also confirmed from UV to visible ratio.

Keyword: Zinc oxide, sol-gel spin coating technique, crystalline size, optical properties.

Introduction and Experimental

Zinc oxide has exhibited properties as an alternative semiconductor to TiO₂ photo electrode because ZnO has some supreme properties compared to TiO₂ such as high electron mobility, easy to synthesis different nanostructures including nano rod, nano wall, nano pillar for increasing dye loading and also has a direct band gap with high binding energy (60 meV) [1]. In a decade, the varieties of ZnO nanostructure is synthesized and are used to construct DSSCs by different growth method such as chemical vapor deposition, electrochemical method, spray pyrolysis and sol-gel spin coating technique. Among these methods, the sol-gel spin coating is low cost and easy method to form a uniform surface of the thin film hence in the present study.

The coating precursor was contained 0.3M zinc acetate in isopropanol and monoethanolamine (MEA) used as stabilizers. The molar ratio of salt and MEA was 1:1. The coating solution was continuously stirred in magnetic stirrer for two hours to get a homogeneous solution and then the solution was heated at 60°C to get a gel form the solution. Before coat film on a glass plate, it was cleaned by chromic acid, acetone and de-ionized water. The thin films were coated at various rotations per minute (RPM) such as 2000 and 2500 RPM. The coated films were pre-heated at 350°C for 10 minutes to remove the existing solvent. These processes were repeated three times. Finally, all the films were annealed 350°C to 450°C for one hour.
Results and discussion

Figure 1 (a, b) shows SEM the images of prepared thin films at various RPM. One can be observed the morphology changes as changing RPM. The agglomerate particles are noticed in figure (1a) whereas small unshaped mount like structure and cracks are observed, when film prepared at 2000 RPM. The particle sizes have varied between 97 to 140 nm. When the RPM increases up to 2500, the morphology of the film has changed from agglomerate particle to cordillera like structure and the size of the crack is increased [2]. The breadths of the cordillera structures are varied from 774 to 991 nm. The surfaces of the cordillera like structure are rough as in inset figure (1b). On this surface, the particle size varied in between 76 to 129 nm.

![Fig. 1 (a, b) shows an SEM image of the sample at different RPM: (a) 2000 and (b) 2500.](image1)

![Fig. 2 shows XDR pattern of thin films prepared at different RPM: (a) 2000 and (b) 2500.](image2)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Particle size (nm)</th>
<th>Dislocation density $\times 10^{14}$</th>
<th>Strain $\times 10^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>43.77</td>
<td>6.76</td>
<td>1.58</td>
</tr>
<tr>
<td>b</td>
<td>43.57</td>
<td>3.95</td>
<td>1.18</td>
</tr>
</tbody>
</table>

**Table 1.** Micro structural parameters of ZnO thin films

The XRD patterns of ZnO micro structures prepared at various RPM is shown in fig. 2. All the diffraction peaks are well indexed to wurtzite hexagonal structure ZnO thin film (JCPDS 01-076-0704). The intensity of the predominant peak (002) is shown high in thin film prepared at 2000 RPM which indicates that the prepared thin films agglomerated particles are grown along c-axis to the substrate. Further increasing RPM to 2500, the structural conversion has taken place in the prepared ZnO thin film from an agglomerated particle to the cordillera structure. The more predominant peak (101) shows high intense, this is an indication of cordillera structure is grown parallel to the substrate. The particle size is calculated from Scherrer formula and values are tabled in table 1. The particle sizes of the prepared thin films are remaining constant, which represents that the increasing RPM is only influences the morphologies and much not affected the growth of the particle size.
Figure 3 shows Raman spectra of the prepared samples. There are four modes present in prepared thin film $E_2$ (low), $A_1$ (TO), $E_2$ (high) and $E_1$ (LO) respectively. The peaks $E_2$ (LO) at 163 cm$^{-1}$ is assigned due to heavy vibration of Zn sub-lattice [3]. The peaks $E_{2L}$-$E_{2H}$ are located at 330 cm$^{-1}$ which is due to the occurrence of multi photon process and second orders Raman scattering. The predominant peaks $E_2$ (high) of non-polar phonon are attributed to first order Raman scattering and vibration of Oxygen atom. The peaks $E_1$ (LO) at 578 cm$^{-1}$ is generally ascribed due to defects such as Oxygen vacancies or Zn interstitials. The peaks located at 388 cm$^{-1}$ is due to $A_1$ transverse optical mode in agglomerated particles [4].

Fig.3 and 4 show Raman and Photoluminescence spectrum (a) 2000 and (b) 500 RPM.

In figure 4, the emission peak at 390 nm is due to recombination of the exciton in UV region. The slight shift is occurred in cordiller like structure compared to agglomerate particle which may be interstitial Zinc in ZnO crystal lattice. The peaks located at 410, 443, 493 and 520 nm correspond to blue- green emission which is due to Oxygen vacancies and Zn interstitial [5]. The peak at 595nm is associated with the presence of OH group and oxygen related defect such as oxygen interstitial, oxygen vacancy in yellow emission [6]. In this present work, we calculated the UV to VIS ratios 1.41 for agglomerated particles and 1.32 for cordiller like structure. From these ratios, we can be ascertained that agglomerated particle is exhibited well crystal quality and low defect concentration.

Conclusion

Zinc oxide thin films have been prepared by the sol - gel technique at various RPM. Structural analysis has been carried out by X-ray diffraction pattern. The morphological changes have been observed from scanning electron microscope. Crystal’s quality has been investigated by micro Raman spectroscopy. The emission properties have been studied by PL spectra.

References


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