This paper investigates the electrochemical behaviour of ZnO films deposited on Cu substrate form a simple aqueous Zinc nitrate solution. ZnO films with grain sizes between 22 and 28 nm are formed by controlling the growth rate. The obtained fibres were uniform, pinhole free and strong adherent to the substrate. XRD, EDAX, SEM and optical properties of the film were also studied.

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1. Introduction

Thin films of zinc oxide is the object of quickly growing in the last few years because of its resistivity control and transparency in the visible wavelength, high electrochemical stability, direct band gap and absence of toxicity[1,2]. Other essential properties of a practical solar selective coating are low cost, ease of mass production[3], stability at operating temperatures and good resistance to thermal shockes, oxidation,[4] UV radiation, [5]humidity and handling.

ZnO thin films have been prepared by a wide varity of techniques such as pulsed laser deposition, sputtering, and electrodeposition[6]. In particular, the electrodeposition [7] method has advantages over other processes because of its simplicity, low equipment cost and the possibility in making large area thin films [8-12]. However, the grain of such Zno electrodeposited from aqueous solution is micron-sized. Recently, the use of nanostuctured substances has been proposed as a way to improve the device performance in light-collecting devices such as solar cells [13-14]. The design of nanostuctured surfaces coated with extremely thin-absorber should lead to the minimization of the optical losses and to the enhancement of the carrier transfer from the active region to the contacts [15]. Thorough nanocrystalline ZnO films can be obtained by electrodeposition from non-aqueous solution. This means high cost, and the method is not simple and not suitable for some applications. In the present work the In incorporation into electrochemically deposited ZnO thin films is further studied and its influence on their physical properties (specifically structural and optical properties) is investigated[16,17].

2. Experimental details

ZnO films electodeposition process were already described elsewhere. The cathodic electrodeposition was made potentiostatically from he electrolyte consisting of 0.1 M Zn(NO₃)₂.

All samples were grown at the temperatures of 40°C, 60°C, 70°C and 80°C using a specific electrode. The time duration for the sample deposited on the copper substrate is 1 hour. Low cost copper sheet were used as substrate. The electrodeposition was measured in a saturated
electrode. The anode consists of 99.99% pure zinc sheets. Samples were obtained with a constant thickness of varying between 1 and 4micron. After a certain time, precipitation starts to take place in the solution. This precipitation may result in a very poor optical quality so the deposition must be stopped before this happens.

The chemical atomic composition of the film was obtained from powder X-ray diffraction (XRD) spectra of the films recorded with a Philips PW3710 diffractometer using CuKα radiation. The instrumental broadening was measured using an n-type silicon(100) monocrystalline sample. The band gap energy $E_g$ was determined by its first derivative peak position.

3. Results

3.1 Grain sizes and surface morphology

Fig. 1. XRD patterns of ZnO film prepared at different current densities

Fig 1a & 1c shows the XRD results for samples grown at different electrodeposition potentials are increasing. The major different peaks corresponding to hexagonal ZnO were found in almost all the samples and are labeled in these figures. Different peaks of the copper substrate also appear.

The grain sizes from the (002) X-ray diffraction peak width, using Scherrer’s formula were in all the cases lesser than 30 nm. This confirms the good crystallinity of the samples. The surface morphology of a typical sample grown at a given electrodeposition potential is presented in Fig. 2. The morphology is found to be similar to the one previously observed for undoped ZnO.
thin films. The resulting crystallites obtained with an electrodeposition potential show a platelet shape, while for the cathodic potentials they showed a cauliflower shape of the SEM. This is an agreement with the very narrow XRD peaks. Furthermore, grains are more densely packed and have fewer holes between them.

Fig. 2. SEM images of ZnO film prepared different current densities

3.2 Optical properties

In Fig. 3 the reflectance spectra (DRS signal) for samples grown at different electrodeposition potentials. The typical spectra, whose XRD shows the presence of ZnO structure. A distinct edge is observed in the interval of wavelength 380 nm - 600 nm.

Fig. 3 The reflectance spectra of ZnO
3.3 Atomic composition

From EDAX measurements the characteristic peaks corresponding to Zn and O are identified. The most important feature of these results is that the main elements present in the film are O and Zn, respectively. Cu peaks appear too, but they are originated mainly from the substrate.

<table>
<thead>
<tr>
<th>Current density (mA /Cm²)</th>
<th>Crystalline size (nm)</th>
<th>Film composition (mass%)</th>
<th>Band gap energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Zn</td>
<td>O</td>
</tr>
<tr>
<td>2</td>
<td>23</td>
<td>33.46</td>
<td>66.54</td>
</tr>
<tr>
<td>4</td>
<td>24</td>
<td>40.22</td>
<td>59.28</td>
</tr>
<tr>
<td>6</td>
<td>25</td>
<td>49.4</td>
<td>50.6</td>
</tr>
<tr>
<td>8</td>
<td>28</td>
<td>47.55</td>
<td>52.45</td>
</tr>
</tbody>
</table>

4. Discussion

XRD and EDAX results reveal the presence of ZnO and copper oxide in the resulting films. The presence of Cu in the ZnO film helps to understand the migration from the substrate in the grain boundaries, then for the smaller grain boundaries less Cu is present in the films. The XRD shows that the only crystalline phase present in the sample is hexagonal ZnO. This shows a clear influence of the electrodeposition potential on the deposited films.

However the SEM images show a surface layer with a different crystallinity in the film surface.

5. Conclusions

ZnO thin films are prepared on copper substrate by cathodic deposition by a simple aqueous solution of Zinc nitrate solution using potentiostatic electrodeposition route. For the suitable growth rate the deposition parameters of ZnO films are studied form the electrolyte of 0.1 M Zn(NO3)2. Nano crystalline grain sizes between 22 to 25 nm are obtained.

References