Fabrication of ZnO nanorods by simplified spray pyrolysis

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Abstract

ZnO layers were deposited by a simple and cost-effective spray pyrolysis using zinc chloride aqueous solutions on glass substrates at 600 °C. The structural properties of nanorods were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM). XRD studies showed that the films were at polycrystalline form and oriented along (002) direction preferentially and other observed orientations were (102), (103) and (004). The standard and the calculated lattice constants are in consistence. It was also observed that the deposited films were ZnO with hexagonal structure and surfaces of the films are found to be nonhomogeneous with hexagonal shaped rods.

Keywords: Nanostructure, simplified spray pyrolysis, ZnO

1. Introduction

Nanostructured materials have attracted considerable interest in recent years due to their potential application in nanoscale electronic and optoelectronic devices. ZnO nanostructures have many applications in solar cells, gas sensors, short-wavelength light-emitting and field effect devices, schottky diodes, coating materials etc. (Devoda et al. 2007a) due to its excellent properties such as wide and direct band-gap of 3.3 eV and high exciton binding energy of 60 meV (Choopun et al. 1999; Guo et al. 2000; Li et al. 2000; Sawada et al. 2002).

ZnO nanostructures have been prepared by various experimental techniques such as a thermal vapor transport method (Cai et al. 2011), spray pyrolysis (Dedova et al. 2007b; Kunlue et al. 2008), chemical vapour deposition (CVD), electrochemical deposition (He et al. 2010), pulsed laser deposition (PLD) (Valerini et al. 2008), sol-gel (Bahadur et al. 2007) etc. Among these techniques, spray pyrolysis is a simple, convenient, low-cost technique for large area coatings (Ravichandran & Philominathan 2008a). Besides this technique has the advantage of ease of adding materials, reproducibility, high growth rate and mass production capability for uniform large area coatings (Serin et al. 2006).

In this study, a further simplified and low cost spray pyrolysis technique using is employed by using a perfume atomizer for the fabrication of ZnO nanostructure. In conventional spray method, usually a carrier gas such as O₂, N₂ or air, is used for spraying the precursor solution. However, in our system, a simplified and inexpensive spray technique using perfume atomizer for atomization is based on hydraulic pressure without using any carrier gas. Perfume atomizers prevents deposition of large droplets, which often take place in conventional spray pyrolysis depositions, enhance wet ability between sprayed micro particles and the previously deposited layers (Ravichandran & Philominathan 2008b; Ravichandran et al. 2009a; Ravichandran & Philominathan 2009b).

2. Experimental Method

The ZnO nanorods reported in the present study were prepared using a cost-effective and simplified spray pyrolysis apparatus (Figure 1). 0.1 M ZnCl₂ aqueous solution was used to deposit on ZnO films. Proposed growth mechanism of the formation of ZnO nanorods from the ZnCl₂ solution can be shown by the following chemical reaction.

\[
\text{ZnCl}_2 + \text{H}_2\text{O} \Rightarrow \text{ZnO} + 2\text{HCl}
\]

Figure 1. Growth mechanism of ZnO thin film
ated substrates were studied. The required temperature before spraying was carried out by X-ray diffraction (XRD) measurement using Rigaku D/Max-IIIC diffractometer with CuKα radiation (λ=1.5418 Å), at 30 kV and 10 mA. The spray interval enables the deposition of the film to attain the temperature before spraying. The spray interval was optimized as 40 cm. The intermittent spray cycle was carried out by using a perfume atomizer. The spray interval was set using a spray controller with a chromel-alumel thermocouple. Distance from the nozzle to substrate was optimized as 40 cm. The intermittent spray cycle followed in this study was a two-step process: the first step was spraying for 1 second and the second step was waiting for 10 seconds. After the deposition, coated substrates were allowed to cool down to room temperature naturally.

The structural characterization of the prepared films was carried out by X-ray diffraction (XRD) measurements using Rigaku D/Max-IIIC diffractometer with CuKα radiation (λ=1.5418 Å), at 30 kV and 10 mA. Surface morphology was examined by TESCAN Vega II LSU model SEM.

<table>
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<tr>
<th>(hkl)</th>
<th>Standard d (Å)</th>
<th>Calculated d (Å)</th>
<th>Standard Lattice constants (Å)</th>
<th>Calculated Lattice constants (Å)</th>
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</thead>
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<td>2.6240</td>
<td>3.250 5.207</td>
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<td>1.4771</td>
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<td></td>
</tr>
<tr>
<td>004</td>
<td>(004)</td>
<td>1.3017</td>
<td>1.3051</td>
<td></td>
</tr>
</tbody>
</table>

The solution was prepared by using a magnetic stirrer that was mixed for 1 h and 30 min subsequently. The prepared clear precursor solution was sprayed onto the pre-heated glass substrates at 600 °C which were cleaned ultrasonically with organic solvents (dimension 1×1×0.1 mm³) using a perfume atomizer. Temperature of the substrates was monitored by employing a temperature controller with a chromel-alumel thermocouple. Distance from the nozzle to substrate was optimized as 40 cm. The intermittent spray cycle followed in this study was a two-step process: the first step was spraying for 1 second and the second step was waiting for 10 seconds. After the deposition, coated substrates were allowed to cool down to room temperature naturally.

The structural characterization of the prepared films was carried out by X-ray diffraction (XRD) measurements using Rigaku D/Max-IIIC diffractometer with CuKα radiation (λ=1.5418 Å), at 30 kV and 10 mA. Surface morphology was examined by TESCAN Vega II LSU model SEM.

3. Result and Discussion

The XRD patterns of the deposited films are shown in Figure 2. XRD image shows that the films are polycrystalline and oriented preferentially along (002) direction. Sonmez et al. (2011) deposited ZnO thin films in (002) direction by spray pyrolysis in 2011. Other observed orientation are (102), (103) and (004). Interplaner distance “d” values were calculated by relation “nλ = 2d sinθ”, where ‘n’ is an integer, ‘λ’ is the wavelength of the x-rays, “d” is the distance between crystal planes and “θ” is the angle between the incident ray and scattering planes.

The calculated “d” values were presented in Table 1 and these values were compared with the standard values from JPCDS card no: 36-1451.

![Figure 2. XRD pattern of ZnO thin film](image)

The matching of the calculated and standard “d” values confirms that the deposited films are ZnO with hexagonal structure. The lattice constants of ZnO with hexagonal structure “a” and “c” were determined by following relation (Ravichandran & Philominathan 2008). Where “d” is the interplaner distance and (hkl) miller indices, respectively. The standard and calculated lattice constants were given in Table 1. The calculated “a” and “c” values agree with JPCDS card no: 36-1451. As seen from Table 1, the standard and the calculated lattice constants are in consistence.

Figure 3 shows the SEM images of the ZnO films. Surfaces of the films are found to be nonhomogeneous with hexagonal shaped rods, which were oriented in different directions. This is in agreement compliance with the XRD results.

![Figure 3. SEM images of ZnO nanorods](image)

4. Conclusions

ZnO nanorods have successfully been synthesized on glass substrates by a simple and the cost-effective spray pyrolysis. Structural analysis revealed that the nanorods were composed of ZnO hexagonal wurzite crystals. From SEM images, the hexagonal shaped rods were oriented in different directions and this conclusion is in compliance with the XRD results.
References


