Study the Effect of Molar Concentration on the Optical and Surface Properties of ZnO Thin Films Prepared by Spray Pyrolysis

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Abstract

Zinc Oxide (ZnO) thin films have been deposited onto glass substrates from different molar concentration of zinc acetate precursor solution using a simple spray pyrolysis technique. The surface morphology, compositional and optical properties of the films has been characterized by Scanning Electron Microscopy (SEM) attached with an EDX and UV spectroscopy. From EDX data, atomic weight % of Zn and O are found to be 60.98 % and 20.37 % respectively. The SEM micrographs of as-deposited film show uniform deposition over the substrate. The absorption coefficient is obtained in the order of $10^6 \text{ m}^{-1}$. For different molar concentrations (0.1M ~ 0.4M), the direct band gap is found to be in the range 3.0 ~ 3.2 eV. The band gap energies depend on molar concentration of solution.

Key words: Spray pyrolysis, ZnO, Molarity, Optical band gap.

Introduction

The growth and characterization of II-VI semiconductor ZnO and ZnO–based alloys has been becoming a more and more active research field in recent years. The research works have been encouraged by both scientific significance and the potential of various practical applications such as light emitting diode (LEDs) and ultraviolet photo detector [Nakamur and Fasol, 1997], UV-blue semiconductor laser [Bagnall et al, 1997], flat panel displays [Ghis et al, 1991], solar cell [Sang et al, 1998], gas sensor [Dayan et al, 1998] and surface acoustic wave devices [Gorla et al, 1999] and so on. ZnO has the largest optical gain ever reports, as well as a high ohmic conductivity. In the recent years, many different techniques such as chemical vapor deposition (CVD) [Gulino et al, 2000], pulsed laser deposition (PLD) [Jin et al, 2000], rf – magnetron sputtering [Kim et al, 2000], atomic layer deposition [Yamada et al, 1999], molecular beam epitaxy (MBE), oxidation of metallic zinc [Cho et al, 1999] have been used to synthesize ZnO thin films. Among the various methods SPD technique provides a simple route of synthesizing thin films because of its simplicity low cost experimental setup. In addition, this technique could be used for the production of large-area thin film deposition without any high vacuum system. This method has good control over the thickness uniformity and good adherence to the substrate. Zinc oxide (ZnO) has been shown to exhibit the large direct band gap (3.37 eV) and exciton binding energy (60 meV) as well as the excellent chemical and thermal stability [Pan et al, 2001; Tian et al, 2003]. From the practical point of view, these properties can severely degrade or modify the performances of a component. Overall, the structural and optical properties of the thin films depend on the method of the preparation. The properties of the films are influenced by the geometry of the experimental setup. From industrial application point of interest, we have deposited ZnO thin films under optimum conditions and studied their surface and optical properties more precisely for various molar concentrations of precursor solution by a locally developed SPD system, so as to reduce the preparation cost and make it economically more viable.

Experimental Details

Spray pyrolysis is basically a chemical process involves spraying aqueous solution onto a substrate held at high temperature. A simple glass nozzle was fabricated to give a fine and very small droplets of precursor solution which is driven by air from the compressor. In the present work, In order to prepare ZnO thin films the aqueous solution of Zinc acetate...
[Zn(CH₃COO)₂.2H₂O] was used as a source of Zn and O respectively. The deposition set up consists of four sections, which include the precursor solution and carrier gas (air) assembly connected to the spray nozzle, the reaction chamber in which the substrate is heated, the pumping and exhausting gas scrubbing systems, and temperature controller with a Copper-Constantan thermocouple to control the substrate temperature. In this study, precursor solutions of 0.1 M ~ 0.4 M concentrations were used as raw material to deposit ZnO thin films. The glass substrates were cleaned ultrasonically in acetone and methanol respectively for 10 minutes in each case. The solution was sprayed onto pre-cleaned glass substrate. The substrate temperature was maintained constant at 573K. The normalized distance between the spray nozzle and the substrate was fixed at 25 cm. The pressure of the carrier gas (air) was kept constant at 1 bar. The solution flow rate was maintained 0.5 ml min⁻¹ throughout the experiment. The films of various thicknesses were prepared through different molar concentrations for fixed deposition time. The possible chemical reaction that takes place on the heated substrate to produce ZnO as follows:

\[
\text{Zn(CH}_3\text{COO)}_2.2\text{H}_2\text{O} \xrightarrow{300 \degree C} \text{ZnO} + \text{CO}_2 + \text{CH}_4 + \text{Steam}
\]

Characterization

The surface properties of the films were examined by using HITACHI S-3400N model Scanning Electron Microscope (SEM) attached with an EDX to measure quantitatively the sample stoichiometry. The Optical transmission measurements were carried out within the wavelength range 300 to 1100 nm using UV-1601 PC SHIMADZU scanning double beam spectrophotometer. The experimental accuracy of the transmittance is (±0.005%) and wavelength is (±0.005%). The observed transmittance data were corrected relative to optically identical uncoated glass substrate. The thicknesses of the films were determined by using Fizeau-fringes method.

Results And Discussion

Surface Morphology

Deposited pure ZnO films are found uniform and well covered on the glass substrate surface. In figure 1 SEM photograph reveals that sprayed particles (atoms) are adsorbed onto the glass substrate into clusters as the primary stage of nucleation and appears as spheroid shape. Under higher magnifications, clusters appear as nano fiber around the nucleation center. Similar feature was also reported by [Llicana et al, 2006] with indium doping. The fibers are becoming unclear with increase of molar concentration. All the fibers vanishes and a smooth surface is observed as shown in figure 1(d).

Figure 1. SEM micrograph of ZnO film for (a) 0.1 M (b) 0.2 M (c) 0.3 M (d) 0.4 M
Compositional studies

The quantitative analysis of the as-deposited ZnO films carried out by EDX is shown in figure 2. Table 1 shows the composition of elements in film in the sprayed solution. Table 2 shows quantitative results of pure ZnO thin films from EDX analysis. The composition of ZnO films were confirmed by energy dispersive X-ray spectroscopy (EDX). Two different peaks corresponding to Zn and one O in the spectrum, which confirms the ZnO thin film. A strong peak is observed which corresponds to Si due to substrate. At high operating voltage the electron beam penetrates the film and reaches the glass surface, which makes Si peak. EDX result reveals that the deposited films are very close to the nominal composition.

Table 1. Atomic% of different compositions of ZnO thin films.

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Zn (0.1 M) atomic%</th>
<th>O (0.1 M) atomic%</th>
<th>Total (0.1 M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>50</td>
<td>50</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 2. Quantitative results of pure ZnO thin films from EDX analysis.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt%</th>
<th>At%</th>
<th>([\text{Zn}] / [\text{O}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>81.68</td>
<td>60.98</td>
<td>2.99</td>
</tr>
<tr>
<td>O</td>
<td>6.68</td>
<td>20.37</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>11.64</td>
<td>18.65</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>100</td>
<td></td>
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</tbody>
</table>

Optical Properties

Variation of optical absorption coefficient with photon energy for various molar concentrations of ZnO films are shown in Figure 4. The absorption coefficient \(\alpha\) is calculated from the transmittance spectrum using the relation

\[ \alpha = -\frac{\ln T}{t} \]

Where \(T\) is the transmittance and \(t\) is the thickness of the film. It shows that the absorption coefficient increases slowly at the higher wavelength region and then increases sharply near the absorption edge. The band gap was determined using the following relation:

\[ \alpha = \frac{A(\hbar \nu - E_g)^2}{h \nu} \]

Where \(A\) is a constant, \(\alpha\) is the absorption coefficient and \(n = 1/2\) for allowed direct transition and \(n = 2\) for allowed indirect transition. Plots of \((\hbar \nu)^2\) versus \(h \nu\) are shown in Figure 5. The direct band gap energy of ZnO has been obtained from the intercept of the straight line drawn from \((\hbar \nu)^2\) versus \(h \nu\) curve on the energy axis. Table 3 indicates that direct band gap decreases with increase of molar concentration of the precursor material. It could be due to the increase of density of localize state in the conduction band.
1.5 as well as surface morphology have been studied for different molar concentrations (0.1M – 0.4M). The SEM micrographs of as-deposited film show homogenous deposition over the substrate. It is observed that the band gap decreases with the increase of the molar concentration of the ZnO thin films. The optical band gap was found to vary from 3~3.2 eV. The band gap could be tuned by controlling the molar concentration of the precursor solutions. The optical results show the suitability of these thin films as optical window material for photovoltaic applications. These results are in good agreement with other reported values. In conclusion, we can state that the spray pyrolysis could be a good and convenient method for the preparation of suitable thin films for scientific studies and technological applications.

### Table 3. Variation of bandgap with molar concentration of ZnO thin film

<table>
<thead>
<tr>
<th>Sample</th>
<th>Molar Concentration</th>
<th>Direct band gap energy, $\Delta E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>0.1 M</td>
<td>3.20</td>
</tr>
<tr>
<td></td>
<td>0.2 M</td>
<td>3.13</td>
</tr>
<tr>
<td></td>
<td>0.3 M</td>
<td>3.10</td>
</tr>
<tr>
<td></td>
<td>0.4 M</td>
<td>3.00</td>
</tr>
</tbody>
</table>

### References


