Synthesis and Structural Properties of Co Doped CuO Thin Films by Spray Pyrolysis

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Abstract: Cobalt doped cupric oxide (CuO) thin films have been deposited onto glass substrate using a spray Pyrolysis technique at different doping concentration. X-ray diffraction patterns for pure and Co doped CuO thin films have monoclinic crystal structure without any extra peaks. The lattice parameters of films increase with increasing Co doping indicating Co substituting in CuO samples. The average crystallite size was determined by Scherrer’s formula and found that crystallite size of the films in the range of 6 to 8 nm. The volume of unit cell of thin films increases with increasing Ni doping. The dislocation densities of the prepared films were reduced with increasing Co doping.

Keywords: CuO; doping; spray pyrolysis; thin films; strain.

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I. Introduction

CuO thin films have attracted special attention because of their fascinating properties. Thus it could accomplish much more passion in the research field for its numerous potential application possibilities. Controlled thickness, size and shape are the primary factor in controlling the physical properties which are crucial for their potential applications. In improving magnetic, an optoelectronics property, CuO thin films has attracted immense attention with the single phase n-type semiconductors. Cupric oxide (CuO) is a p-type semiconductor with a narrow energy band gap (1.6 to 2.2 eV) [1-2]. The CuO have monoclinic crystal structure. The CuO is also a promising material due to its huge applications such as gas sensors, solar energy, diode fabrication, lithium ion batteries, electrochemical cells, superconductor, photovoltaic, nano-electronics and spintronics [3-6]. Doping of CuO with transition magnetic ions introduces intensified properties facilitating the formation of DMS. A few researchers to develop DMS based CuO films [7]. Numerous methods have been used to fabricate CuO, including pulsed laser deposition [8], spin-coating [9], thermal evaporation [10], microwave combustion [11], chemical vapour deposition [12], microwave irradiation[13], successive ionic layer adsorption and reaction (SILAR) [14], molecular beam epitaxy [15], and dipcoating techniques [16]. Compared with other deposition techniques, spin-coating is especially efficient, due to its high deposition rate and low cost. In this paper, we report the synthesis and structural properties of Co doped CuO thin films by a spray pyrolysis. The lattice parameters, volume, strain, dislocation density and average crystallite size have been calculated. The effects of Co doping on structural properties of the CuO thin films have been studied.

II. Experimental

In CuO thin film was deposition by using chemical spray pyrolysis techniques. Before deposition take accurate weight of substrate by using “Standard Microbalance Weight Measurement” and mark it as I, II, III. The initial solution is prepared from Cupric Acetate and Cobalt acetate of conc. 0.1 M. Add this solution to the substrate holder for spraying. Above marked substrate is kept on a heater and adjust different temperature ranges 350-400 °C. Using spray machine 20 ml solution can be spared on glass substrate and give a solution air pressure. After completion of spacing note spray rate and cooling substrate at room temperature for good crystallized films and take out substrate from machine and take a weight of deposited film.

<table>
<thead>
<tr>
<th>Spray parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc. Of Cupric Acetate solution and Co Acetate</td>
<td>0.1 M</td>
</tr>
<tr>
<td>Nozzle to substrate distance</td>
<td>23 cm</td>
</tr>
<tr>
<td>Solution flow rate</td>
<td>4 ml/min</td>
</tr>
<tr>
<td>Gas pressure</td>
<td>3 Kg/cm²</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>350-400 °C</td>
</tr>
</tbody>
</table>

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III. Result and discussion

The XRD diffraction patterns for films deposited onto glass substrate are shown in figure 1. All samples show highly (111) orientated. The samples deposited at 573 K substrate temperature seem to have the good crystallinity. The XRD patterns show monoclinic crystal structure of pure and Co doped CuO thin films and without any extra impurities. The diffraction peaks at 35.4 and 38, and a low intensity peak at 66 were corresponds to (002), (111), and (-311) planes respectively.

![XRD pattern of pure and Co doped CuO thin films.](image)

**Figure 1.** XRD pattern of pure and Co doped CuO thin films.

In addition, the XRD patterns showed that the films were polycrystalline in nature. The peak positions shifted to lower angle with increasing Co doping concentration indicating that Co substituting in CuO host matrix. The Ni doping did not change the monoclinic crystal structure as shown in the XRD patterns. The Scherrer’s equation was used to estimate the average crystallite size of Co and pure CuO thin films from the XRD patterns. The average crystallite size was calculated using Scherrer’s equation is given by

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

Here, D is crystallite size, \(\lambda\) is the X-ray wavelength (Cu Kα; 1.5405 Å), \(\beta\) is full width at half maximum (FWHM) in radians, \(\theta\) is the Bragg’s angle in degrees, K is the correction factor and D is the crystallite size. The calculated crystallite size for pure and Co doped CuO thin films are in the range of 6 -8 nm. As the doping concentration of Co increased, the crystallite size for the strong peaks increased. This shows that the size of all films changes with Co doping. It may be due to the small grain growth of Co doped CuO thin films as compared to the pure CuO samples.

The obtained dislocation densities decreased from \(2.66 \times 10^{16}\) to \(2.40 \times 10^{16}\) lines/m² with increase in Co content. The strain for pure CuO samples was small as compared to Co doped CuO thin films. It may be due to increase in crystallite size with Co doping concentration. The decrease in strain indicates the decrease in lattice imperfections and formation of high quality films [18].

Where \(\delta\) is the dislocation density, \(D\) is the crystallite size, \(\varepsilon\) is the strain of the deposited films determined from the following equation [17]:

\[
\varepsilon = \frac{\beta}{4 \tan \theta}
\]
The lattice parameters were calculated from XRD data and found that for pure CuO were a=4.6896 Å, b=3.4175 Å and c=5.1126 Å and Co doped CuO are a=4.7662 Å, b=3.4615 Å and c= 5.1134 Å respectively. The volume of unit cell was calculated following equation:

\[ V = abc \sin \beta \]

IV. Conclusions

The effect of Co doping in a spray pyrolysis process of CuO thin films was investigated. XRD study reveals that both pure and Co doped CuO thin films have monoclinic crystal structure. The lattice parameters and volume of unit cell as function of Co doping concentration were calculated from the XRD patterns. The average crystallite size for Co doped samples large as compared to the pure CuO samples. A strain decrease with increasing Co doping indicates the decrease in lattice imperfections and formation of high quality films. The dislocation density for doped films was small as compared to the pure CuO films due to the increasing crystallite size. Based on this study, prepared films were suitable for solar cells and nanodevices applications.

References