Co doping induced structural and optical properties of sol–gel prepared ZnO thin films

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ARTICLE INFO

Article history:
Received 15 November 2013
Received in revised form 14 June 2014
Accepted 20 June 2014
Available online 27 June 2014

Keywords:
ZnO
Co:ZnO
Thin film
Ultrasonic spray pyrolysis

ABSTRACT

The preparation conditions for Co doping process into the ZnO structure were studied by the ultrasonic spray pyrolysis technique. Structural and optical properties of the Co:ZnO thin films as a function of Co concentrations were examined. It was observed that hexagonal wurtzite structure of ZnO is dominant up to the critical value, and after the value, the cubic structural phase of the cobalt oxide appears in the X-ray diffraction patterns. Every band-edge of Co:ZnO films shifts to the lower energies and all are confirmed with the PL measurements. Co substitution in ZnO lattice has been proved by the optical transmittance measurement which is observed as the loss of transmission appearing in specific region due to Co2+ characteristic transitions.

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1. Introduction

Zinc oxide (ZnO) is a II–VI compound semiconductor with a wide direct band gap of 3.37 eV at room temperature. In addition to the electrical and optical properties of undoped ZnO, the transition metal doped ZnO forms are promising candidate materials in the field of spintronics (spin-electronics). Various methods such as pulsed laser deposition [1], chemical vapor transport [2], electrodeposition [3], co-precipitation [4] and solid-state reaction [5], and spray pyrolysis [6] can be used to synthesize ZnO. Among these methods, spray pyrolysis technique can be applicable without vacuum environment; of course, this technique is cheap and displaying comparable properties and competitive functionality with that produced by other techniques. The research has been increased on the ternary semiconductors such as transition metal doped ZnO owing to its high Curie temperature for the ferromagnetic transition calculated in bulk materials and found to be around 300 K [7–10].

Co doping creates a considerable change in the band gap of ZnO [11–14], but this variation has been reported as an increase in some other research and as a decrease in the band gap for ZnO in other research. This case indicates the uncertainty. A reason for this can be structural defects in the ZnO crystal lattice as well as because of the vacancies in the crystal structure or interstitials [15]. The uncontrolled cases as the structural defects and/or impurities that arise as growing the film affects the bonding nature, charge transfer and the band structure in the material. This makes it very difficult to obtain reproducible device performance and reliability. Some authors reported in the literature that red-shift is attributed to the sp–d exchange and some other authors observed that blue-shift is attributed to the Burnstein–Moss effect considering the Co concentration. When the volume solubility limit in two-component and multicomponent alloys has reached a certain concentration, the first phase remains constant and then the extra phases appear. In order to determine the solubility limit, one has to follow the change of the lattice spacing and concentration obtained from the X-ray diffraction (XRD) and SEM-EDS spectrum, respectively. There is uncertainty about solubility limit for Co doped ZnO. Lee et al. [16] reported that the doped Co ion was fully substituted into a ZnO lattice at 5 mol%, but the secondary phase of the Co2O4 was formed above 5 mol% of Co doping. However, other reports [17,18] have indicated that Co can be incorporated in the matrix of ZnO up to 7–10 at% without forming any second phase. All these reports thus indicate that Co has a limited solubility in ZnO up to 10 at%. In contrast to this, Rath [19] observed that all the peaks match well with the wurtzite structure of ZnO in both pure and Co doped ZnO samples up to a cobalt concentration of 20%.

In this study, we aimed to contribute to clarify the uncertainty for band gap shift. That is why, we investigate the structural and optical properties of ZnO and Co:ZnO (CZO) thin films that were

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Table 1

The atomic percentage of oxygen, zinc and cobalt in the Co:ZnO thin films obtained from EDS measurements.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Molarity of Co (M)</th>
<th>Normalized atomic weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O</td>
<td>Zn</td>
</tr>
<tr>
<td>CZO1</td>
<td>0.01</td>
<td>42.6</td>
</tr>
<tr>
<td>CZO2</td>
<td>0.02</td>
<td>36.9</td>
</tr>
<tr>
<td>CZO3</td>
<td>0.03</td>
<td>42.4</td>
</tr>
<tr>
<td>CZO4</td>
<td>0.04</td>
<td>38.6</td>
</tr>
<tr>
<td>CZO5</td>
<td>0.05</td>
<td>43.6</td>
</tr>
</tbody>
</table>

2. Material and methods

ZnO and Co:ZnO (CZO) thin films were deposited onto glass substrates using the ultrasonic spray pyrolysis (USP) method as a function of Co concentration.

2.2. Structural properties

The X-ray patterns for Co:ZnO thin films at room temperature and reference peak positions are presented in Fig. 1a. The results pointed out showed that there is no impurity and/or unreacted phase of ZnO and Co considering the reference peak positions, (1 0 0), (0 0 2), (1 0 1), and (1 0 3) peaks of ZnO were observed. However, (1 1 1) and (2 0 0) peaks at 36.9° and 42.7° Bragg angle of cobalt oxide, respectively, were observed. The starting molarity up to 0.03 M of precursor solution included Co, (0 0 2) peak of hexagonal wurtzite structure becomes more intensive comparing with other peaks (Fig. 1b). In these films, up to 0.03 M, the hexagonal wurtzite structure of ZnO seems to be protected. In the doping process, it is observed that there is a limitation of Co doping into the ZnO structure. The molarity is then greater and/or equal to the 0.03 M value, (2 0 0) peak which belongs to the cubic structure of cobalt oxide which then starts to occur. This limit value is confirmed using EDS measurements. Table 1 summarizes the relative chemical content of the oxygen, zinc and cobalt present in the films as a function of content of the cobalt acetate tetrahydrate inserted in the starting solution. We observed that the Co substituted Zn site up to 12% (Fig. 1c) which corresponded to 0.03 M without showing any extra phase in XRD spectra. Peaks corresponding to the glass substrate elements such as Si and Ca were also detected. The (0 0 2) peak indicating a strong orientation along the c-axis of ZnO with hexagonal wurtzite structure is replaced by (2 0 0) orientation with the cubic structure as Co molarity increases. The peak position of (0 0 2) shifts...
to the higher Bragg angle, and also the calculated c-lattice parameter decreases due to the increasing Co concentration in the ZnO structure (Fig. 2). But the intensity of (2 0 0) peak decreases when Co is doped into the ZnO structure with the molarity value of more than 0.04 M.

### 3.2. Optical properties

The optical transmission spectra of ZnO and Co doped ZnO thin film samples are shown in Fig. 3. The effects of Co doping into the ZnO lattice are clearly observed in the optical transmission spectra. The increase of Co concentration in the ZnO structure decreases the optical transmittance and imparts deep green color to the samples (Fig. 4). In addition, increasing Co concentration also modifies optical transmittance for the specific region due to Co$^{2+}$ characteristic transitions. These transitions also suppress the interference fringes in this region of Co:ZnO films if the film thickness is sufficient to create interference fringe. In order to eliminate the influence of differences in sample thickness, normalized transmittance to the value at 800 nm were taken into account. The absorption peaks, indicated with arrows in Fig. 3, centered at 571 nm (2.18 eV), 619 nm (2.01 eV) and 662 nm (1.88 eV), are related to characteristic features of d–d transition of Co$^{2+}$ ions. They are assigned to transition from $^4A_2$ (F) state to $^2E$ (G), $^4T_1$ (P) and $^4A_1$ (G) states, respectively [15]. This is a clear evidence to prove the existence of Co at the tetrahedral sites of the ZnO hexagonal wurtzite structure as Co$^{2+}$. Comparing the ionic radii of Co$^{2+}$ (0.058 nm) which is very close to ionic radii of Zn$^{2+}$ (0.060 nm) and the absorption peaks we can conclude that the Co atomically substitutes on Zn sites. This is also confirmed in many groups, which included a variety of methods and optical absorption [15,18,20–22].

![Fig. 2](image1.png) Structural parameters of Co:ZnO thin films according to the XRD results vs Co molarity; for c-lattice parameter (“•” symbol) and diffraction angle 2θ for (002) peak (“□” symbol).

![Fig. 3](image2.png) Normalized experimental optical transmission spectra for Co:ZnO thin films according to transmission value at 800 nm.

![Fig. 4](image3.png) Experimental optical transmission spectra (solid line) of 0.02 M Co content in starting solution for Co:ZnO thin film: Also the theoretical optical transmission spectra (“○” symbol) are shown for comparison.

**Table 2**

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Molarity of Co (M)</th>
<th>$t$ (nm)</th>
<th>$n$ (532 nm)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>0.00</td>
<td>75 ± 2</td>
<td>1.73</td>
<td>3.33</td>
</tr>
<tr>
<td>CZO1</td>
<td>0.01</td>
<td>105 ± 2</td>
<td>2.23</td>
<td>3.072</td>
</tr>
<tr>
<td>CZO2</td>
<td>0.02</td>
<td>95 ± 2</td>
<td>2.42</td>
<td>3.061</td>
</tr>
<tr>
<td>CZO3</td>
<td>0.03</td>
<td>160 ± 2</td>
<td>2.73</td>
<td>2.985</td>
</tr>
<tr>
<td>CZO4</td>
<td>0.04</td>
<td>170 ± 2</td>
<td>2.63</td>
<td>3.020</td>
</tr>
<tr>
<td>CZO5</td>
<td>0.05</td>
<td>180 ± 2</td>
<td>2.59</td>
<td>3.030</td>
</tr>
</tbody>
</table>

The optical transmission spectrum can be used in the determination of the optical constants of the thin film deposited onto the transparent substrate. When the product of the refractive index and film thickness of the film have allowed the formation of interference fringes, classical methods such as the envelope method developed by Swanepoel [23] can be used. As well as the number of the interference fringes and depth of the fringes are crucial to perform this method. However, Pointwise Unconstrained Minimization Algorithm (PUMA) [24] and many other iterative methods [25] can be used when the interference fringes observed or not observed in the transmission spectrum. Considering the normal dispersion relation, the refractive index decreases with the increasing wavelength. This is not valid for the Co:ZnO thin films for the region where the loss of transmission due to Co$^{2+}$ characteristic transitions which modulate the transmittance spectrum of our samples is observed. Therefore, we used PUMA technique for this limited region which starts from the inflexion wavelength to the wavelength corresponding first characteristic transition which is centered at 571 nm (2.18 eV). Inflexion wavelength is defined from second derivative of optical transmission curve [6,26]. There is an excellent agreement between the experimental spectra and theoretical spectra for all the samples and one of the experimental and computed optical transmission spectra for the Co:ZnO thin film are shown in Fig. 4. Calculated film thickness and refractive index for 532 nm are given in Table 2. The value of refractive index is passing through a maximum considering the Co concentration such as...
structure, red shift is observed in the absorption edge due to the sp-d exchange interactions between the band electrons and the localized d-electrons of the Co$^{2+}$ ions substituting Zn$^{2+}$ ions. Calculated value of the optical band gap with increasing Co molarity from 0 to 0.05 M is given in Table 1.

Fig. 6 shows the PL spectra of as-grown samples. Photoluminescence spectra of the samples have been recorded at room temperature. The PL emission in the UV bands was observed. Band-edge transitions as well as direct-band transitions for ZnO at around 380 nm (3.26 eV) are observed. Gaussian fitting was performed on the PL spectra of the samples containing Co. Among the two peaks one is centered around 400 nm ($\lambda_1$) assigned to the band gap transition and the other peaks assigned to the near-band-edge (NBE) emission are centered at 407 nm, 415 nm, 418 nm, 407 nm and 413 nm for the samples CZ01, CZ02, CZ03, CZ04 and CZ05, respectively (Table 3). Band gap values are decreasing up to a threshold value of Co concentration. This behavior is also observed in the refractive index variation. In addition, the observed PL intensity began to decrease when the cobalt was introduced into the ZnO structure.

4. Conclusion

The structure and optical properties of Co doped ZnO films were studied with respect to cobalt concentration in the starting solution in which the cobalt acetate tetrahydrate was used as a Co source. Our studies show that Co doping affects ZnO lattice immediately. When the Co molarity is greater than the 0.03 M or Co concentration obtained from EDS analysis is about 12%, the ZnO (0 0 2) peak intensity decreases and CoO (2 0 0) peak intensity increases with increasing Co concentration. Co substitution in ZnO lattice has been proved by the optical transmittance measurement, whereas it is not clearly seen in the XRD diffractogram for the CZ01 and CZ02 sample. The optical transmittance decreases with increasing Co concentration. ZnO is white colored because it does not absorb any
visible light. When the Zn\textsuperscript{2+} ions are replaced with Co\textsuperscript{2+} ions in the ZnO lattice, the films absorb visible light, and the color of the films turn to deep green. The character of the band gap of the CZO films is direct type with cobalt doping. When the cobalt doping is increased, Tauc plots are becoming a more rounded in shape and the inflexion point moves to the longer wavelengths. The band gap obtained from Tauc’s plot shifting toward to the longer wavelengths was verified with room temperature PL measurement. The band gap narrowing can be attributed to the conduction band and the valence band shifted downward and upward, respectively. We concluded that the red-shift is typically attributed to the sp–d exchange between the ZnO band electrons and localized d-electrons associated with the doped Co\textsuperscript{2+} cations.

Acknowledgement

This study was supported by The Scientific Research Unit of Mehmet Akif Ersoy University with project numbers 110-NAP-10, 0172-NAP-13, and 0173-NAP-13.

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