Isotropic Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+δ}$/Ag high temperature superconducting wires

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ON THE COVER: High temperature superconducting (HTS) materials are widely used in modern cables, magnets, motors, transformers, fault current limiters, superconductor magnetics energy storages, etc. by virtue of their high critical current density ($J_c$) and feasible operation at liquid nitrogen temperature. Researchers from Tsinghua University have fabricated multi-filamentary Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+y}$/Ag HTS round wires by powder-in-tube method; and by optimizing the mechanical deformation process, they increase both the core density and the $J_c$ significantly. Moreover, they also exhibit an effective way to enhance the local 2223 filament texture. For more details, see the article by Peng Xie et al. on pp. 105–114.

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Structural and optical investigations of In doped ZnO binary compound

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ABSTRACT
The structural and optical properties of indium (In) doping in zinc oxides (ZnO) are investigated. Chemical spray deposition technique is used for doping ZnO by In. X-ray diffraction (XRD) studies have shown a change in preferential orientation from (002) to (101) crystal plane with increasing in In dopant concentration. The transmission spectra, absorption coefficient, energy band gap, refractive index and optical dielectric constant utilizing specific models for In doped ZnO are investigated. The measured and calculated results are in agreement with experimental and theoretical data.

Keywords: ZnO, Chemical Synthesis, Optical Properties, Doping, Analysis.

1. INTRODUCTION
Zinc oxide has attracted interest due to its electronic properties, i.e., semiconducting band gap is about 3.4 eV, and the possibilities of application in optoelectronics, directly or as a substrate for the growth of other semiconductors such as GaN and SiC is available.1 Moreover, because of its superior electronic, optical and piezoelectric properties, it is an attractive candidate for applications in ultraviolet light emitters, transparent field-effect transistors, ultraviolet nanolasers, photodetectors, surface acoustic wave devices, sensors and piezoelectric devices.2–4 Low resistive zinc oxides have been achieved by doping with different group-III elements like Al, B, In and Ga or with group-VII elements like fluorine.5 The essential phase of crystallization for ZnO is hexagonal wurtzite phase.6–8 Theoretical7 and experimental9 studies have been focused on ZnO, with an interest to study the properties of ZnO in its cubic phase.9 In the last few years there were tremendous efforts on understanding the physical and optical properties of ZnO with particular attention on fabrication devices such as UV lasers.10

Rezapour and Talebian11 have synthesized crystalline ZnO with different morphologies by solvothermal and sol-gel synthesis methods in various solvents as the reaction medium. X-ray diffraction (XRD) data has shown hexagonal single-phase ZnO with the wurtzite crystal structure for all solvents. The optical properties of synthesized ZnO were investigated by UV-vis absorption and room temperature photoluminescence (RTPL) and well-defined relationship with solvent viscosity. Photocatalytic activity (PCA) of ZnO with different morphologies has been examined toward photodegradation of phenol by the same group.11 Also, Lu et al.12 have investigated the optical transmittance of Al-doped ZnO improved using ZnO nanorods prepared by the aqueous chemical growth method, where the length and diameter of the rods were controlled by the OH− concentration of hexa-methenamine in the solution.
They have improved the transmittance of Al-doped ZnO with post-grown ZnO nanorods at wavelengths between 400 and 850 nm by modulating the air volume ratio of rod densities and diameters.

Spray pyrolysis technique has been profited due to its simplicity and possibility to produce large areas. The properties of the deposited material can be varied and controlled by proper optimization of spraying conditions. The purpose of this work is to investigate the effect of In-doped ZnO on the structural and optical properties. The organization of this work is as the following: Section 2 displays the experimental process. The structural and optical properties are stated in Section 3. Last one is the conclusion.

2. EXPERIMENTAL PROCESS
In doped ZnOs were deposited on glass substrates using spray pyrolysis technique. The deposition method involves the decomposition of an aqueous solution of zinc acetate. To achieve indium doping, indium trichloride (InCl₃) was added to the solution. The In/Zn ratio was varied from zero to 1.6 at.%. The resulting solution was sprayed onto heated substrate held at 723 ± 5 K. The upper limit for doping concentration was fixed at 1.6 at.%. Compressed air was used as the carrier. To enhance electrical conductivity as-deposited, it was annealed at 573 K for 90 min under a vacuum of 10⁻⁵ mbar. From zinc acetate solutions having molarity 0.2 and 0.4 M were also deposited at optimum doping level keeping the other process parameters constant. The apparatus and the deposition details have already been reported.

Thicknesses were measured using the multiple beams interferometric technique. The structure of the samples was studied using XRD. (Philips PW 1710). The optical transmission studies were carried out using Ultra-Violet (UV-vis) spectroscopy, (Shimadzu UV-240) in the range 300–900 nm.

3. RESULTS AND DISCUSSION
3.1. Structural Properties
The XRD patterns of In doped ZnO with different In concentrations deposited at substrate temperature of 723 ± 5 K using 0.1 M zinc acetate solution is shown in Figure 1. All the peaks in the pattern correspond to hexagonal structure of ZnO. No phase corresponds to indium/indium oxide or other indium compounds were detected by XRD. Significant changes are observed in XRD patterns which have shown a decrease of peak intensity corresponding to (002) crystal plane, increase of peak intensity corresponding to (101) crystal plane and disappear (112) crystal plane due to increasing doping concentration. Undoped effect was reported in the literature which has shown that 5 at.% In doping will lead to the formation of samples with preferential orientation along (101) crystal plane.

The lattice constants found from the most prominent peaks in the diffraction patterns of ZnOs for different doping concentrations are given in Table I. The lattice constants are found to be in good agreement with experimental and theoretical results. Figure 2 shows the XRD pattern of 0.8 at.% In doped ZnO prepared at 723 ± 5 K using zinc acetate precursor solutions of different molarities. All the peaks in the diffraction patterns coincide well with the patterns observed for hexagonal structure of ZnO powder sample. All the samples prepared at 0.8 at.% In doping concentration exhibited c-axis orientation which is found improved with increasing in molarity of the spraying solution. The lattice constants measured from the most prominent peaks in the diffraction patterns of In doped ZnO using zinc acetate precursor solutions of 0.8 at.% of different molarities are given in Table I. The measured lattice constants, a and c, are in good agreement with experimental value and theoretical one.
Table I. Lattice constants of In doped ZnO deposited at 723 K using zinc acetate solutions of different concentrations (first part) and of different molarities (second part).

<table>
<thead>
<tr>
<th>In dopant concentration (at.%)</th>
<th>(a) (Å)*</th>
<th>(c) (Å)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M</td>
<td>3.249</td>
<td>5.205</td>
</tr>
<tr>
<td>0.4</td>
<td>3.247</td>
<td>5.206</td>
</tr>
<tr>
<td>0.8</td>
<td>3.253</td>
<td>5.210</td>
</tr>
<tr>
<td>1.2</td>
<td>3.251</td>
<td>5.208</td>
</tr>
<tr>
<td>1.6</td>
<td>3.261</td>
<td>5.208</td>
</tr>
<tr>
<td>0.8 at.%</td>
<td>3.247</td>
<td>5.206</td>
</tr>
<tr>
<td>Molarity of solution (M)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>3.253</td>
<td>5.210</td>
</tr>
<tr>
<td>0.2</td>
<td>3.242</td>
<td>5.202</td>
</tr>
<tr>
<td>0.4</td>
<td>3.240</td>
<td>5.200</td>
</tr>
</tbody>
</table>


3.2. Optical Properties

The transmittance and optical band gap of zinc oxides prepared using 0.1 M zinc acetate solution for different dopant concentrations are given in Table II. The upper limit for doping concentration was fixed at 1.6 at.% of In as deposited at higher doping concentrations were of less transmittance. The transmittance and optical band gap of 0.8 at.% In doped ZnO prepared at substrate temperature 723 ± 5 K, using precursor solutions of different molarities are given in Table II. The investigated energy gap at 0 at.% shows good agreement with experimental value[18] and better than theoretical ones.[19] The transmittance is decreased due to increasing of growth rate with concentration of the spraying solutions. It is expected that the high growth rate induces other atmospheric impurity contamination to be lower and incorporation of zinc at interstitial sites to be greater.[20]

The optical transmission spectra of zinc oxide prepared at substrate temperature 723 ± 5 K, for different indium concentrations is shown in Figure 3. The high transmittance is a direct consequence of the wide band gap. The transmittance is found to decrease at 1.2 at.% In doping concentration. The decrease of transmittance at higher doping concentrations may be due to the increased scattering of photons by crystal defects created by doping. The free carrier absorption of photons may also contribute to the reduction of optical transmittance.[21] The absorption coefficient is deduced from the transmission spectrum using the relation,

\[
\alpha = \ln(1/T)/t \tag{1}
\]

where \(T\) is the transmittance and \(t\) is the thickness. The optical band gap was calculated using \((\alpha hv)^2\) versus \(hv\) graph.

Figure 4 shows the typical variation of \((\alpha hv)^2\) versus \(hv\) for 0% and 0.8 at.% In doped ZnO deposited at 723 ± 5 K using 0.1 M zinc acetate solution. As mentioned upon, the optical band gap is increased from 3.24 to 3.28 eV with In doping concentration from 0 to 1.6 at.% (see Table II). The transmission spectra of 0.8 at.% In doped ZnO deposited at substrate temperature 723 ± 5 K using zinc acetate precursor solutions of different molarities is shown in Figure 5. The decreasing in transmittance at higher molarities is due to increase of thickness.[13] The optical band gap was found to be 3.29 eV for the deposited using precursor solutions of molarity 0.2 and 0.4 M as given in Table II.

The refractive index \(n\) is a very important physical parameter related to the microscopic atomic interactions. The refractive index will be related to the density and the local polarizability of these entities.[22] Consequently, many attempts have been made in order to relate the
Table II. Transmittance, energy gap, refractive index and optical dielectric constant of In doped ZnO (~175 nm thickness) prepared at 723±5 K using zinc acetate solutions of different concentrations (first part) and of different molarities (second part).

<table>
<thead>
<tr>
<th>In dopant concentration (at.%)</th>
<th>Transmittance at 550 nm (%)</th>
<th>$E_g$ (eV)</th>
<th>$n$</th>
<th>$\varepsilon_\infty$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M</td>
<td>98</td>
<td>3.24 1.57</td>
<td>2.039 2.279 1.052 2.008</td>
<td>4.157 5.193 1.106 3.72</td>
</tr>
<tr>
<td>0.4</td>
<td>96</td>
<td>3.26 1.57</td>
<td>2.026 2.273 1.0519 2.008</td>
<td>4.104 5.166 1.104 3.72</td>
</tr>
<tr>
<td>0.8</td>
<td>94</td>
<td>3.27 1.57</td>
<td>2.020 2.271 1.0511 2.008</td>
<td>4.080 5.157 1.104 3.72</td>
</tr>
<tr>
<td>1.2</td>
<td>86</td>
<td>3.27 1.57</td>
<td>2.020 2.271 1.0511 2.008</td>
<td>4.080 5.157 1.104 3.72</td>
</tr>
<tr>
<td>1.6</td>
<td>70</td>
<td>3.28 1.57</td>
<td>2.014 2.268 1.0508 2.008</td>
<td>4.056 5.143 1.104 3.72</td>
</tr>
<tr>
<td>Molarity of solution (M)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1 M</td>
<td>94</td>
<td>3.27 1.57</td>
<td>2.020 2.271 1.0511 2.008</td>
<td>4.080 5.157 1.104 3.72</td>
</tr>
<tr>
<td>0.2</td>
<td>80</td>
<td>3.29 1.57</td>
<td>2.008 2.265 1.0504 2.008</td>
<td>4.032 5.130 1.103 3.72</td>
</tr>
<tr>
<td>0.4</td>
<td>76</td>
<td>3.29 1.57</td>
<td>2.008 2.265 1.0504 2.008</td>
<td>4.032 5.130 1.103 3.72</td>
</tr>
<tr>
<td>0.8 at.%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


Ravindra et al. had been presented a linear form of $n$ as a function of $E_g$:

$$n = \alpha + \beta E_g$$

(2)

where $\alpha = 4.048$ and $\beta = -0.62$ eV$^{-1}$. Herve and Vandammel proposed an empirical relation as follows:

$$n = \sqrt{1 + \left(\frac{A}{E_g + B}\right)^2}$$

(3)

where $A = 13.6$ eV and $B = 3.4$ eV. For group-IV semiconductors, Ghosh et al. have published an empirical relationship based on the band structure and quantum dielectric considerations of Penn and Van Vechten:

$$n^2 - 1 = \frac{A}{(E_g + B)^2}$$

(4)

where $A = 8.2E_g + 134$, $B = 0.225E_g + 2.25$ and $(E_g + B)$ refers to an appropriate average energy gap of the material. The refractive indices of the end-point compounds are investigated and listed in Table II.

This is verified by the calculation of the optical dielectric constant $\varepsilon_\infty$ which depends on the refractive index.

Fig. 3. Optical transmission spectra of In doped ZnO deposited at a substrate temperature of 723±5 K using 0.1 M zinc acetate solution for different concentrations: (1) 0%, (2) 0.4 at.%, (3) 1.2 at.% and (4) 1.6 at.%.

Refractive index and the energy gap $E_g$ through simple relationships. However, these relations of $n$ are independent of temperature and incident photon energy. Here the various relations between $n$ and $E_g$ will be reviewed.

Fig. 4. Typical variation of $(\omega h\nu)^2$ versus $h\nu$ of In doped ZnO deposited at 723±5 K using 0.1 M zinc acetate solution for different concentrations (a) 0% and (b) 0.8 at.%.
Note that $n_e = n^2$. It is clear that the investigated refractive indices $n$ at 0\% are in agreement with the experimental value. Ravindra et al. model shows that it is appropriate for In doped ZnO in enhancing the optoelectronics efficiency. This work is an impetus to investigate other theoretical researches experimentally.

4. CONCLUSION

The spray pyrolysis method gives best quality of In doped ZnO. The spray deposition of 0.8 at.\% indium doped zinc acetate (0.1 M) solution at substrate temperature 723 ± 5 K is found to be optimum for deposition of good quality. The deposited compound at optimum conditions gives a transmittance of 94\% at 550 nm of 0.1 M solution. The structural properties of lattice constants show agreed results in comparison with experimental and theoretical data. The optical transmittance correlates inversely with doping and Ravindra et al. model of refractive index that proves its suitability for optoelectronics efficiency.

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