TO: CORRESPONDING AUTHOR

AUTHOR QUERIES - TO BE ANSWERED BY THE AUTHOR

Dear Author

Please address all the numbered queries on this page which are clearly identified on the proof for your convenience.

Thank you for your cooperation

| No Queries |

Production Editorial Department, Taylor & Francis
4 Park Square, Milton Park, Abingdon OX14 4RN

Telephone: +44 (0) 1235 828600
Facsimile: +44 (0) 1235 829000
Photoconductivity and photoluminescence in chemically deposited films of (Cd–Zn)S:CdCl₂, Ho

S. BHUSHAN* and S. PILLA

SOS in Physics, Pt Ravishankar Shukla University, Raipur (C.G.) 492010, India

(Received 13 September 2006; revised 23 March 2007; in final form 3 April 2007)

Results of SEM, XRD, optical absorption/reflectance, photoconductivity (PC), and photoluminescence (PL) are presented for (Cd–Zn)S:CdCl₂, Ho films prepared by chemical deposition technique by direct dipping either at room temperature (RT) or at 60 °C in a water bath. SEM studies show the presence of non-uniform distribution of particles. XRD studies show lines of CdS, ZnS along with lines of CdCl2 and Ho. PL is found to be pronounced in films of RT preparation and for those prepared at 60 °C, PC is higher. Optical absorption/reflectance studies show the presence of Ho corresponding to the transition 5F₁ → 5G₃. Emissions corresponding to the transitions 5S₂/3F₄ → 5L₄, 5G₃ → 3I₄, and 3I₅ → 3I₄ are observed in PL emission spectra.

Keywords: 72.40 Photoconduction; 81.15L Deposition from liquid phases (melts and solutions); 78.55 Photoluminescence

1. Introduction

Studies on films of CdS-type materials are important because of their wide applications as sensitive photoconductors, IR. detectors, solar cells, etc. Thus, it is always worthwhile to prepare highly photosensitive materials. Studies on photoluminescence (PL) are also quite important due to their tremendous applications as lamp phosphors and display devices. Earlier workers employed sophisticated techniques like vacuum evaporation, spray pyrolysis, sputtering, and molecular beam epitaxy methods [1] for the preparation of films of such materials. Bhushan et al. [2–8] used chemical deposition technique and reported quite high photo-to-dark current ratios, strong PL, and moderate photovoltaic effects in such films. The utility of chemical deposition method in the deposition of metal chalcogenide thin films was reviewed by Mane and Lokhande [9]. Bhushan et al. also observed AC electroluminescence in some of the films [10]. They used La, Pr, Nd, Sm, Gd, and Dy as impurities and found quite high photo response due to these impurities. Further, it was also found that CdCl₂ helps in promoting crystallization of CdS [11]. Triple valence Ho exhibits an interesting energy level scheme with well-separated energy levels providing privilege for radiative transitions and thus

*Corresponding author. Tel.: +91-771-2262864 (O)/+91-771-2262838 (R); Email: bhushan_312006@rediffmail.com

ISSN 1042-0150 print/ISSN 1029-4953 online © 2007 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/10420150701380051

Techset Composition Ltd, Salisbury GRAD237894 TeX Page#: 15 Printed: 19/6/2007
has been found to be a very suitable element in upconversion system [12]. These upconversion processes are interesting as they are useful in optical devices such as temperature sensors, IR quantum counter detectors, three different color emitting phosphors, compact visible or UV solid state lasers, etc. [13, 14]. Ho has also been found useful as a wavelength calibration material in molecular absorption spectroscopy on the basis of their spectral coverage and absorption band shape [15]. Due to these reasons, Ho was selected as an impurity and CdCl₂ as a material to help crystalline growth. This paper reports the results of photoconductivity (PC) and PL in chemically deposited (Cd–Zn)S: CdCl₂, Ho films, not reported earlier. Interesting results of PC rise and decay studies, PC excitation spectra, PL emission spectra, optical absorption spectra/specular reflectance spectra, XRD and SEM studies are presented and discussed.

2. Experimental techniques

2.1 Film preparation

The films were prepared on cleaned substrates of microscopic glass slides/Al plates of dimensions 24x75 mm². The substrates were cleaned with acetone and distilled water and were dipped vertically in a mixture of 1 M cadmium acetate + zinc acetate (in appropriate ratio) and thiourea, triethanolamine and 30% aqueous ammonia, 0.01 M CdCl₂ (all solutions prepared in double distilled water), and Ho₂O₃ (since being insoluble in distilled water, was dissolved in dilute H₂SO₄, and molar concentrations varied from 0.001 to 0.05 M). All the chemicals were of analytical grade (minimum purity 99.9%). The pH value of the mixture in the absence of Ho was around 11.0, which reduced to 8.3 in its presence. Films were prepared either at 60°C in water bath or at RT. RT preparation needed longer dipping. The deposition of films is based on the precipitation followed by condensation. In the beginning when precipitation started, stirring was done. After that, the deposition was made in the static condition. After deposition, films were cleaned with distilled water and then dried by keeping the films in open atmosphere at room temperature. The thickness of the films were measured by interference method and was found to be in the range of 0.4694–0.4949 μm for different (Cd–Zn)S films deposited using water bath at 60°C for 1 h, in the range of 0.6994–0.7112 μm for those deposited at RT for 19 h on glass substrates, and in the range of 0.5611–0.5733 μm for films deposited on Al substrates (at 60°C using water bath for 1 h).

2.2 PC and PL cells

For PC studies, coplanar electrodes (1.5 mm wide and 24 mm long at a separation of 2 mm) were formed by applying colloidal silver paint to the surface of the film. The photocurrents were measured by exposing the total area of the film. The PL cell consisted of the film deposited on the substrates.

2.3 Measuring instruments

PC excitation source was an incandescent bulb of 100 W (power 18 mW) for PC rise–decay studies and of 1 KW for PC excitational spectral studies. For recording the photocurrent, a nanometer (DNM-121) was used. The PL excitation source was a high pressure Hg source from which 365 nm radiation was selected for excitation purposes by using a Carl Zeiss interference filter. For detection of emitted light, an RCA 6217 photomultiplier tube, operated
by a highly regulated power supply (EHT-11, scientific Equipments, Roorkee), was used. The integrated light output in the form of current was recorded by a sensitive polyflex galvanometer (10⁻⁹ A/mm). For the studies of PL emission spectra and PC excitation spectra, a prism monochromator was used. For the study of optical absorption spectra/reflectance spectra, a Shimadzu (UV-VIS) Pharmaspec-1700 spectrophotometer was used. XRD and SEM studies were performed at IIT, Guwahati, using models D8 Advance Bruker AXS (German) and LEO 1430VP, respectively.

3. Results and discussion

3.1 SEM studies

The SEM micrographs of (Cd₀.₈-Zn₀.₂)S: CdCl₂, Ho films are shown in figure 1. Figure 1 a and b presents the morphological features of the film for the top region at 5500×, and in figure 1c and d, the morphological features of the film for the central region are shown at 5500× and 3500×, respectively. From all these micrographs, non-uniform distribution of particles is observed. It consists of either some single particles or cluster of particles. In one of the micrographs, the average particle sizes of some of the particles (Pa₁ = 496.2 nm and Pa₂ = 546.0 nm) are also mentioned.

3.2 XRD studies

The X-Ray diffractograms of (Cd–Zn)S: CdCl₂, Ho prepared on glass and Al substrates are shown in figures 2 and 3, respectively. The corresponding data are presented in tables 1 and 2 for the two cases, respectively. From the data of table 1, it is clear that the diffraction lines such as (111)ₑ, (200)ₑ, (220)ₑ, (102)ₕ, (103)ₕ, (311)ₑ, (222)ₑ, and (202)ₕ of CdS along with (111)ₑ, (200)ₑ, (105)ₑ, (106)ₑ, (102)ₕ, and (10 12)ₑ of ZnS are assigned, two lines of CdCl₂, namely (009)ₑ and (021)ₑ, along with (200)ₑ line of Ho are also observed. In addition to these, one line due to Cd [(101)ₑ ] and Ni₄Cl [(111)ₑ] each are also assigned. The assignments were made by comparing with ASTM data and calculation of lattice constants and their comparison with the reported values. The XRD patterns of the films prepared on Al substrate consist of (111)ₑ and (103)ₑ lines of CdS along with (220)ₑ of ZnS. Diffraction lines (002)ₑ, (100)ₑ, (101)ₑ, and (102)ₑ of Cd are also assigned along with (110)ₑ of Al₂O₃ and (200)ₑ of Ho.

3.3 Optical absorption spectra/specular reflectance spectra

The optical absorption spectra of different (Cd–Zn)S films prepared on glass substrates are shown in figure 4. From their Tauc's plots (extrapolation of plots between (αhv)² vs. hv), it is found that with increase in concentration of ZnS, the band gap increases. On addition of CdCl₂, a slight change in the band gap is observed. In Ho-doped films, a broad peak in the region 450-510 nm is seen, which is associated with the presence of Ho (shown by arrow). Ishizaka and Yurokawa [16] have recently reported that, in the absorption spectra of Ho³⁺-doped alumina films, a peak at ~450 nm appears due to the transition ⁵F₁ → ⁵G₅ in Ho. In the present case, a diffraction line due to (200)ₑ of Ho is also assigned. This shows that Ho goes into the lattice of (Cd–Zn)S, which is indicated by its presence in XRD patterns and absorption spectra. The Tauc's plot, from the observed values of absorption in the presence of Ho, gives band gap = 2.6 eV. However, from the absorption values obtained from the dotted
Figure 1. SEM micrographs of (Cd_{0.8}Zn_{0.2})S:CuCl_{2} Ho film prepared on Al substrate. (a) and (b) Top region of film at 5500x; (c) and (d) central region of film at 5500x and 3500x, respectively.
Table 1. XRD data of (Cd$_{0.8}$-Zn$_{0.2}$)S: CdCl$_2$, Ho prepared on glass substrate.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Observed</th>
<th>Reported</th>
<th>Rel intensities</th>
<th>(hkl)</th>
<th>Lattice constant (Å)</th>
<th>Observed</th>
<th>Reported</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>3.3616</td>
<td>3.36</td>
<td>100</td>
<td>100</td>
<td>(111)$_{CdS}$</td>
<td>a = 5.822</td>
<td>a = 5.818</td>
</tr>
<tr>
<td>2</td>
<td>3.0831</td>
<td>3.12</td>
<td>19.2</td>
<td>100</td>
<td>(111)$_{ZnS}$</td>
<td>a = 5.2013</td>
<td>a = 5.406</td>
</tr>
<tr>
<td>3</td>
<td>2.9635</td>
<td>2.90</td>
<td>27.76</td>
<td>40</td>
<td>(200)$_{CdS}$</td>
<td>a = 5.927</td>
<td>a = 5.818</td>
</tr>
<tr>
<td>4</td>
<td>2.8369</td>
<td>2.705</td>
<td>71.5</td>
<td>10</td>
<td>(200)$_{ZnS}$</td>
<td>a = 5.6338</td>
<td>a = 5.406</td>
</tr>
<tr>
<td>5</td>
<td>2.7602</td>
<td>2.76</td>
<td>22.9</td>
<td>2</td>
<td>(105)$_{ZnS}$</td>
<td>a = 3.8159</td>
<td>a = 3.82</td>
</tr>
<tr>
<td>6</td>
<td>2.5816</td>
<td>2.575</td>
<td>9.3</td>
<td>47.5</td>
<td>Wurtzite (8H)</td>
<td>c = 25.0162</td>
<td>c = 24.96</td>
</tr>
<tr>
<td>7</td>
<td>2.5103</td>
<td>2.52</td>
<td>16.8</td>
<td>2</td>
<td>Wurtzite (8H)</td>
<td>a = 5.163</td>
<td>a = 5.15</td>
</tr>
<tr>
<td>8</td>
<td>2.4604</td>
<td>2.450</td>
<td>11.7</td>
<td>25</td>
<td>(102)$_{CdS}$</td>
<td>a = 3.8159</td>
<td>a = 3.82</td>
</tr>
<tr>
<td>9</td>
<td>2.3191</td>
<td>2.345</td>
<td>14.4</td>
<td>100</td>
<td>(101)$_{Ho}$</td>
<td>a = 5.259</td>
<td>a = 5.618</td>
</tr>
<tr>
<td>10</td>
<td>2.2868</td>
<td>2.273</td>
<td>12.84</td>
<td>20</td>
<td>(102)$_{ZnS}$</td>
<td>a = 6.335</td>
<td>a = 6.26</td>
</tr>
<tr>
<td>11</td>
<td>2.2394</td>
<td>2.238</td>
<td>13.96</td>
<td>4</td>
<td>Wurtzite (10H)</td>
<td>a = 3.8787</td>
<td>a = 3.876</td>
</tr>
<tr>
<td>12</td>
<td>2.1623</td>
<td>2.0800</td>
<td>17.3</td>
<td>2</td>
<td>(101)$_{ZnS}$</td>
<td>a = 3.8159</td>
<td>a = 3.82</td>
</tr>
<tr>
<td>13</td>
<td>2.058</td>
<td>2.056</td>
<td>26.3</td>
<td>80</td>
<td>(220)$_{CdS}$</td>
<td>a = 5.8209</td>
<td>a = 5.818</td>
</tr>
<tr>
<td>14</td>
<td>1.945</td>
<td>1.943</td>
<td>12.3</td>
<td>12</td>
<td>(009)$_{CdCl_2}$</td>
<td>a = 4.1262</td>
<td>a = 4.1354</td>
</tr>
<tr>
<td>15</td>
<td>1.8696</td>
<td>1.897</td>
<td>5.1</td>
<td>12</td>
<td>(103)$_{CdCl_2}$</td>
<td>a = 6.5827</td>
<td>a = 6.7120</td>
</tr>
<tr>
<td>16</td>
<td>1.7539</td>
<td>1.753</td>
<td>17.9</td>
<td>60</td>
<td>(311)$_{CdS}$</td>
<td>a = 5.817</td>
<td>a = 5.818</td>
</tr>
<tr>
<td>17</td>
<td>1.5917</td>
<td>1.6801</td>
<td>4.3</td>
<td>12</td>
<td>(222)$_{CdS}$</td>
<td>a = 5.8255</td>
<td>a = 5.818</td>
</tr>
<tr>
<td>18</td>
<td>1.6598</td>
<td>1.658</td>
<td>8.02</td>
<td>12</td>
<td>(021)$_{CdCl_2}$</td>
<td>a = 3.8510</td>
<td>a = 3.842</td>
</tr>
<tr>
<td>19</td>
<td>1.5808</td>
<td>1.581</td>
<td>1.92</td>
<td>7</td>
<td>Wurtzite (10H)</td>
<td>c = 17.459</td>
<td>c = 17.489</td>
</tr>
<tr>
<td>20</td>
<td>1.508</td>
<td>1.509</td>
<td>8.1</td>
<td>42</td>
<td>(002)$_{Ho}$</td>
<td>a = 4.1262</td>
<td>a = 4.1354</td>
</tr>
<tr>
<td>21</td>
<td>1.495</td>
<td>1.482</td>
<td>10.3</td>
<td>5</td>
<td>(001)$_{CdCu}$</td>
<td>c = 6.7839</td>
<td>c = 6.7120</td>
</tr>
</tbody>
</table>

Temperature of preparation: 60°C; duration: 1 h.

Table 2. XRD data of (Cd$_{0.8}$-Zn$_{0.2}$)$_2$S: CdCl$_2$, Ho prepared on Al substrate.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Observed</th>
<th>Reported</th>
<th>Rel intensities</th>
<th>(hkl)</th>
<th>Lattice constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.3645</td>
<td>3.36</td>
<td>3.79</td>
<td>100</td>
<td>(111)$_{CdS}$</td>
</tr>
<tr>
<td>2</td>
<td>2.808</td>
<td>2.809</td>
<td>31.4</td>
<td>65</td>
<td>(002)$_{Ho}$</td>
</tr>
<tr>
<td>3</td>
<td>2.5838</td>
<td>2.580</td>
<td>21</td>
<td>32</td>
<td>(100)$_{Cd}$</td>
</tr>
<tr>
<td>4</td>
<td>2.57949</td>
<td>2.5749</td>
<td>18.8</td>
<td>47.5</td>
<td>(200)$_{Ho}$</td>
</tr>
<tr>
<td>5</td>
<td>2.3724</td>
<td>2.3789</td>
<td>8.32</td>
<td>40</td>
<td>(110)$_{Al_2O_3}$</td>
</tr>
<tr>
<td>6</td>
<td>2.347</td>
<td>2.345</td>
<td>100</td>
<td>100</td>
<td>(101)$_{Cd}$</td>
</tr>
<tr>
<td>7</td>
<td>1.9013</td>
<td>1.9010</td>
<td>25.2</td>
<td>32</td>
<td>(102)$_{Cd}$</td>
</tr>
<tr>
<td>8</td>
<td>1.9048</td>
<td>1.912</td>
<td>47</td>
<td>51</td>
<td>(200)$_{ZnS}$</td>
</tr>
<tr>
<td>9</td>
<td>1.8990</td>
<td>1.8979</td>
<td>20.4</td>
<td>42</td>
<td>(103)$_{CdS}$</td>
</tr>
</tbody>
</table>

Temperature of preparation: 60°C; duration: 1 h.

The band gap is found to be 2.49 eV. This value is quite close to the band gap obtained in the absence of Ho (2.46 eV).
Regarding the films prepared on Al substrate, it was not possible to observe the absorption spectra. The corresponding specular reflectance spectra were studied for bare Al substrate as well as for different (Cd–Zn)S films, and the corresponding results are shown in figure 5. Generally, the reflectance intensity will be weak if the absorption is strong at a certain wavelength. Therefore, the reverse curve of the reflectance spectra can correspond to the absorption state. In the present case, the reflectance of Al shows a slight increase from 300–320 nm and then remains a constant up to 700 nm. Comparing the reflectance spectra of (Cd–Zn)S, (Cd–Zn)S: CdCl₂, and (Cd–Zn)S: CdCl₂, Ho, with that of Al, mainly the following observations are made:

1. The reflectance in (Cd–Zn)S, (Cd–Zn)S: CdCl₂, and (Cd–Zn)S: CdCl₂, Ho films are higher. The reflectance in the former two materials is almost similar whereas that in the presence of Ho, slightly higher reflectance is observed, which is in accordance with the decrease in absorbance in the presence of Ho.

2. In Ho-doped film, a slight decrease in reflectance in the spectral region near 450 nm is observed, which is in accordance with the increase in absorption in this region.

3. In the shorter regions, some peaks are observed, which may be due to the presence of different materials, but in the absence of reflectance data, it is not possible to relate them to particular elements.

The (Cd–Zn)S: CdCl₂, Ho film prepared on Al substrate showed different PL emission spectra, particularly the central region showed emission color in lower wavelength side. The reflectance spectra of the corresponding three regions (top, central,
Figure 3. X-ray diffractogram of (Cd_{0.8}-Zn_{0.2})S:CdCl$_2$, Ho film prepared on Al substrate at 60°C.

Figure 4. Absorption spectra of different (Cd-Zn)S films prepared on glass substrates at 60°C (a) (Cd$_{0.9}$-Zn$_{0.1}$)S; (b) (Cd$_{0.8}$-Zn$_{0.2}$)S; (c) (Cd$_{0.7}$-Zn$_{0.3}$)S; (d) (Cd$_{0.8}$-Zn$_{0.2}$)S:CdCl$_2$; (e) (Cd$_{0.8}$-Zn$_{0.2}$)S:CdCl$_2$, Ho.

and bottom) are shown in figure 6. The general nature seems to be similar along with lowering of reflectance in the spectral region near 450 nm, which may be due to Ho.
3.4 PC rise and decay studies

The PC rise and decay curves of different (Cd–Zn)S films are shown in figure 7. Due to the variation of zinc content, maximum photocurrent was observed for 0.7:0.3 combination of CdS to ZnS under visible excitation. With this combination, the volume of CdCl₂ was varied, and the maximum current was recorded for 6 ml volume. Similarly, the content of Ho₂O₃ was also varied, and the maximum photocurrent was observed for a volume of 2 ml. PC response was studied for the films prepared at RT and in water bath at 60°C. The effect of IR irradiation was also studied for films prepared in water bath. The photoresponse was more for films prepared under IR irradiation whereas at RT, it was comparatively lower, as shown in figure 8. As stated...
Figure 7. PC rise and decay curves of different (Cd-Zn)S films prepared on glass substrates at 60°C. (Cd_{0.7}-Zn_{0.3})S; \Delta, (Cd_{0.7}-Zn_{0.3})S:CdCl_2; \times, (Cd_{0.7}-Zn_{0.3})S:CdCl_2, Ho.

later, PL in films prepared at RT shows better emission, and hence lower PC is expected in such films, as PL and PC behave oppositely. The values of $I_{pc}/I_{dc}$ ratio, trap depths, lifetime, and mobility were evaluated by methods discussed in earlier publications [4]. The values of $I_{dc}, I_{pc}, (I_{pc}/I_{dc})$, trap depths, lifetime, and mobility for films prepared at 60°C are summarized in table 3. From the table, it is observed that the values of lifetime and mobility both increase in the presence of impurities, which may be a main cause of photosensitization.

The PC excitation spectra of different (Cd_{0.7}-Zn_{0.3})S films are shown in figure 9. It was also observed that due to increasing concentration of ZnS, the peak positions of PC excitation spectra shifted toward shorter wavelength side. A small change in peak positions, and hence the corresponding band gaps are also seen. The corresponding data and their comparison with the values obtained from optical absorption spectra are presented in table 4.

3.5 PL spectra

Changes in band gap due to addition of ZnS have already been reported in the absorption spectra. Corresponding changes were also observed in the PL emission spectra. Maximum emission intensity was observed in (Cd_{0.8}-Zn_{0.2})S, and hence this combination was used for PL studies. In the presence of flux, at its different concentrations, the highest emission appears at a volume of 2 ml CdCl_2. Therefore this concentration was used. The PL emission spectra of different (Cd-Zn)S and (Cd-Zn)S:CdCl_2 films prepared on glass substrates at different concentrations are shown in figure 10.
Figure 8. PC rise and decay curves of different (Cd$_{0.7}$-Zn$_{0.3}$)S: CdCl$_2$, Ho films prepared on glass substrates at 60°C. △ at RT; □ in water bath; ⊙ IR irradiation during preparation in water bath.

Table 3. Values of $I_d$, $I_{pc}$, $I_{pc}/I_{dc}$, lifetime ($\tau$), mobility ($\mu$) and trap depth ($E$) for different (Cd-Zn)S films.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Sample</th>
<th>$I_d$ (nA)</th>
<th>$I_{pc}$ (μA)</th>
<th>Gain $I_{pc}/I_{dc}$</th>
<th>Lifetime $\tau$ (s)</th>
<th>Mobility-$\mu$ (cm$^2$/V s)</th>
<th>Trap depth ($E$) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(Cd$<em>{0.7}$-Zn$</em>{0.3}$)S</td>
<td>0.15</td>
<td>90</td>
<td>$6 \times 10^5$</td>
<td>37.5</td>
<td>42.6</td>
<td>$E_1 = 0.74769$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$E_2 = 0.77111$</td>
</tr>
<tr>
<td>2</td>
<td>(Cd$<em>{0.7}$-Zn$</em>{0.3}$)S: CdCl$_2$</td>
<td>0.1</td>
<td>124.2</td>
<td>$1.24 \times 10^6$</td>
<td>60</td>
<td>55.1</td>
<td>$E_1 = 0.75434$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$E_2 = 0.77786$</td>
</tr>
<tr>
<td>3</td>
<td>(Cd$<em>{0.7}$-Zn$</em>{0.3}$)S: CdCl$_2$, Ho</td>
<td>0.05</td>
<td>147.5</td>
<td>$2.9 \times 10^6$</td>
<td>73.5</td>
<td>105.2</td>
<td>$E_1 = 0.76250$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$E_2 = 0.78364$</td>
</tr>
</tbody>
</table>

Temperature of preparation: 60°C; duration: 1 h.

PL emission spectra of (Cd-Zn)S: CdCl$_2$, Ho films at different molar concentrations of Ho$_2$O$_3$ are shown in figure 11. It is observed that there is a shift in peak positions on higher wavelength side due to increasing molar concentrations of Ho. Maximum emission appears at 0.01 M concentration. Therefore, this molar concentration was used for different preparations in the presence of Ho. At this molar concentration, the emission spectra were studied at different volumes of Ho$_2$O$_3$ as shown in figure 12. It is observed that maximum emission appears at a volume of 4 ml. Shifting of peaks to higher wavelengths show substitution of Ho in the lattice of (Cd-Zn)S. Lowering in emission intensity at 0.05 M Ho may be due to concentration quenching. The PL emission spectra were studied for films prepared in water bath at a temperature of 60°C and at RT. The maximum PL intensity appeared in films prepared at RT, as shown in figure 13. This may be due to higher thickness in the films prepared at RT.
Changing concentrations of NH₄OH also affected the emission intensity. Such kind of behavior is shown in figure 14, which presents the PL emission spectra at different concentrations of NH₄OH. Alkaline medium provides a better condition for deposition of films, which may be favored at higher concentrations of NH₄OH. This may probably be the cause of higher emission in such films. It is also observed that at higher concentrations of NH₄OH, a peak on the shorter wavelength side appears. The peak at ~541 nm may be due to the transitions from the ^5S₂/^5F₄ states to the ^5I₈ ground state of Ho³⁺, and the lower peak (515 nm) may be related to the ^5G₄ → ^5I₇ transition in Ho [16]. The results of PL emission spectra of Ho-doped films prepared on Al substrate are shown in figure 15. In this case, the different parts of the films showed different emission colors. While the central region showed emission color on the lower wavelength side, the top and bottom regions showed emission on the higher wavelength side. The peak at 501 nm observed in the central region may be attributed to the ^3H₅ → ^5I₈...
Figure 10. PL emission spectra of different (Cd-Zn)S films prepared on glass substrates at 60°C. (Cdo.9-Zn0.1)S; Δ, (Cdo.8-Zn0.2)S; *, (Cdo.7-Zn0.3)S; ○, (Cdo.6-Zn0.4)S: CdCl2 (1 ml); □, (Cdo.8-Zn0.2)S: CdCl2 (2 ml); △, (Cdo.8-Zn0.2)S: CdCl2 (3 ml).

Figure 11. PL emission spectra of different (Cdo.8-Zn0.2)S: CdCl2 Ho films prepared on glass substrates at 60°C at different molar concentrations of Ho2O3. (Cdo.8-Zn0.2)S: CdCl2 Ho, 0.005 M; ○, 0.01 M; □, 0.05 M.
Figure 12. PL emission spectra of different (Cd_{0.8}-Zn_{0.2})S: CdCl\textsubscript{2}, Ho films prepared on glass substrates at 60°C at different volumes of Ho\textsubscript{2}O\textsubscript{3} (0.01 M) •, 2 ml; □, 3 ml; ○, 4 ml; △, 5 ml.

Figure 13. PL emission spectra of different (Cd_{0.8}-Zn_{0.2})S: CdCl\textsubscript{2}, Ho films prepared on glass substrates at 60°C. ◊, in water bath. •, at RT.
Figure 14. PL emission spectra of different (Cd$_{0.8}$Zn$_{0.2}$)$_2$S: CdCl$_2$ Ho films prepared on glass substrates at 60 °C at different concentrations of NH$_4$OH. □, 50%; ∆, 60%; ▲, 70%; ○, 80%; ●, 90%.

Figure 15. PL emission spectra of (Cd$_{0.8}$Zn$_{0.2}$)$_2$S: CdCl$_2$ Ho film prepared on Al substrate at 60 °C. ●, top region of film; ○, central region of film; ▲, bottom region of film.
transition in Ho [16]. Peaks observed in the remaining regions are similar to those prepared on glass substrates.

4. Conclusions

SEM Studies show the presence of non-uniform distribution of particles including single or cluster of particles. XRD patterns show the existence of CdS, ZnS, Cd, CdCl₂, and Ho. Optical absorption studies show the presence of Ho through the transition $^5\text{F}_1 \rightarrow ^5\text{G}_5$. Optical reflectance studies for films prepared on Al substrate also show changes in reflectance due to the presence of Ho. While PC is higher in films prepared at 60°C, PL is pronounced in RT preparation. PL emission spectra are related to the transitions $^5\text{S}_2/^3\text{F}_4 \rightarrow ^5\text{I}_8$, $^5\text{G}_3 \rightarrow ^5\text{I}_7$, and $^3\text{H}_5 \rightarrow ^5\text{I}_6$. Band gaps determined from optical absorption spectra and the PC excitation spectra are found to be almost similar.

Acknowledgements

The authors are thankful to Drs Pratima Agrawal, Manoranjan Kar, and K. Senapati of IIT, Guwahati, for making XRD and SEM studies. One of the authors (S.P.) is also grateful to Dr Abraham Oommen, Exe-Vice Chairman and Dr R.N. Dash, Director of M.P. Christian College of Engineering and Technology, Bilalai, for kindly permitting to continue research work at Pt. R.S.U, Raipur, (C.G.).

References

This is to certify that Ms. Sandhya Pillai, Department of Physics, M. P. Christian College of Engineering & Technology, Bhilai, Durg has attended the IUMRS-ICAM 2007 held at Bangalore during October 8-13, 2007. She has made a POSTER PRESENTATION in this conference.

(S B KRUPANIDHI)
Chair, ICAM 2007
IUMRS-ICAM 2007
TECHNICAL PROGRAMME & ABSTRACTS

10th International Conference on Advanced Materials
(IUMRS-ICAM 2007)

8-13, October, 2007, Bangalore, India
Venue: HOTEL GRAND ASHOK

Organized by in association with

MRSI IISc JNCASR

Website: www.icam2007.com
Photoluminescence in Chemically Deposited Holmium Doped (Cd-Zn)S Films

S. Bhushan1 and S. Pillai2

1S. O. S in Physics, Pt. Ravishankar Shukla University, Raipur, C.G, India
2M. P. Christian College of Engineering & Technology, Bhilai, C.G

Results of SEM, XRD, Optical absorption / Reflectance Spectra and Photoluminescence (PL) emission spectra are presented for (Cd-Zn)S: CdCl2, Ho films prepared on glass and Al substrates by chemical deposition technique either at room temperature (RT) or at 60° C in water bath. SEM studies show the presence of non-uniform distribution of particles. XRD studies show prominent lines of CdS and ZnS along with those of CdCl2 and Ho.

Better crystallinity is observed in films deposited on Al substrates in comparison to those prepared on glass. Optical absorption / reflectance show the presence of Ho corresponding to the transition \( ^{3}I_{8} \rightarrow ^{5}F_{1}, ^{5}G_{6} \). PL is found to be pronounced in films of RT preparation. Strong PL is observed in films deposited on Al substrate compared to those on glass. The PL emission spectra show peaks corresponding to the transitions \( ^{3}S_{2} / ^{3}F_{4} \rightarrow ^{3}I_{8}, ^{5}G_{5} \rightarrow ^{3}I_{7} \), and \( ^{3}H_{5} \rightarrow ^{3}I_{8} \) in Ho.
SHRI SHANKARACHARYA COLLEGE OF ENGINEERING & TECHNOLOGY

A National Level Technical Conference
October 26th & 27th, 2007

Certificate

This is to certify that the paper entitled "Photoluminescence and Photoconductivity of chalcogenide thin films prepared by chemical deposition technique" by Dr./Mr./Ms. Sandhya Pillar has been awarded as the B.E.S.T. paper for the session in the National Conference - Technovision 07, held on 26th & 27th October, 2007, organised by the Dept. of Applied Physics, Shri Shankaracharya College of Engineering & Technology, Bilaspur.

Organizing Secretary
Head of the Department

Please visit our website: www.scet.com
Photoluminescence and photoconductivity properties of Holmium
doped (Cd$_{1-x}$Zn$_x$)$_2$S
films prepared by chemical deposition technique

S. Bhushan * and Sandhya Pillai **
S.O.S. in Physics, Pt. Ravishankar Shukla University, Raipur
** Dept. of Physics, M.P.C.C.T., Bhilai.

Abstract: (Cd$_{1-x}$Zn$_x$)$_2$S: Ho films were prepared by chemical deposition technique by direct
dipping at 60°C in a water bath on glass and Al substrates. Results of SEM, XRD, Optical
Absorption/Reflectance, Photoconductivity (PC) and Photoluminescence (PL) are presented
for such films. SEM studies show the presence of non-uniform distribution of particles. XRD studies
show lines of CdS, ZnS along with lines of CdCl$_2$ and Ho. Films prepared on Al substrate show
better crystallinity. Optical absorption/reflectance show the presence of Ho corresponding to the
transition $^4$I$_8$ $^2$F$_{5/2}$, $^2$G$_{5/2}$ PC and PL are found to be maximum at different concentrations of Ho.
Quite high photo current ($I_{pd}$) to dark current ($I_{pd}$) ratios with a maximum value of the order of 10$^6$
or are observed. This high photosensitization is related to increase in mobility and lifetime due to
photo excitation. PL emission spectra show a shift in peak positions on higher wavelength side due
to increasing molar concentrations of Ho. Emissions corresponding to the transitions
$^2$S$_1$ $^2$F$_{5/2}$ $^4$I$_8$, $^2$G$_{5/2}$ $^4$I$_7$ and $^3$H$_{5/2}$ $^4$I$_8$ in Ho$^{3+}$ are observed. PL emission
spectra of Ho doped films prepared on Al substrate showed different emission colours in different
parts of the film.
This is to certify that Mrs. Sandhya Pillai of MPCCET, BHILAI has participated and presented a research paper entitled Photoconductivity in Chemically Deposited films doped with rare earths in the National Conference (BITCON - 2007) held during 16 - 17 March 2007.
PHOTOCONDUCTIVITY IN CHEMICALLY DEPOSITED FILMS DOPED WITH RARE EARTHS

S. Bhushan * and S. Pillai **
* Prof & Head, S.O.S. in Physics, Pt. Ravishankar Shukla University, Raipur
** Lecturer, Dept. of Physics, M.P.C.C.E.T, Bhatkal.

ABSTRACT
Results of Photoconductivity (PC) rise and decay, PC excitation spectra and Optical absorption spectra are presented for (Cd-Zn)S films prepared in the presence of CdCl₂ as flux and Ho as impurity. The ratio of saturated photocurrent of rise curve (Ip₁) to dark current (Id) has been found to be of the order of 10⁷ in doped films. The values of lifetime and mobility have been found to increase in the presence of impurity. Optical absorption studies indicate the presence of Ho corresponding to the transition \( ^{5}F_{j} \rightarrow \ ^{5}G_{s} \). Values of band gap determined from absorption studies closely match with those obtained from excitation spectral studies.

1. INTRODUCTION
The II-VI semi-conducting compounds, mainly the cadmium chalcogenides, have been found to be quite promising materials in the field of optoelectronics. Besides having their optical gaps corresponding to the visible spectra, they also exhibit band to band type transition. FC studies of films of such compounds are important because of their potential use as sensitive photoconductors, i.R. detectors, Solar cells etc. Earlier workers employed sophisticated techniques like vacuum evaporation, spray pyrolysis, sputtering and molecular beam epitaxy methods [1] for the preparation of films of such materials. Bhushan and co-workers [2-5] used chemical deposition technique and reported quite high photo to dark current ratios, strong PL and moderate photovoltaic effects in such films. The utility of chemical deposition method in the deposition of metal chalcogenide thin films was reviewed by Mane and Lokhande [9]. Bhushan and co-workers also observed A.C. electroluminescence in some of the films [10]. Further, it was also found that CdCl₂ helps in promoting crystallisation of CdS [11] due to which, it was used as flux. The trivalent rare earth ions incorporated into a solid have recently drawn much attention since they show distinct spectral lines of absorption and emission due to the electronic transition within 4fN shell configuration [12]. Bhushan et al have reported quite high photo response in chemically deposited films using rare earth ions like La, Pr, Sm, Nd, Dy and Gd as impurities and in the present case, Ho was used. The energy level scheme of Ho shows well-separated energy levels facilitating radiative transitions and thus has been found to be a very suitable element in up conversion systems [13, 14]. The present paper reports the results of PC in chemically deposited (Cd-Zn)S: CdCl₂, Ho films not reported earlier. Interesting results of FC rise and decay studies, PC excitation spectra, and optical absorption spectra are presented and discussed.

2. EXPERIMENTAL TECHNIQUES:
2.1. Film preparation:
The films were prepared on cleaned substrates of microscopic glass slides of dimensions 24 mm X 75 mm. The substrates were cleaned with acetone & distilled water and were dipped vertically in a mixture of 1M Cadmium acetate + Zinc acetate (in appropriate ratio), Thiourea, Triethanolamine, 30% aqueous Ammonia, 0.01M CdCl₂, and 0.001M Ho₂O₃. All the chemicals were of analytical grade (minimum purity 99.9%). The pH value
mixture varied from 11.0 to 8.3. Films were prepared at 60°C in water bath. The deposition of films is on precipitation followed by condensation. In the beginning when precipitation started, stirring was. After that, the deposition was made in the static condition. After deposition, films were cleaned with water and then dried by keeping the films in open atmosphere at room temperature. The thickness of films was measured by interference method and were found to be in the range of 0.4694 - 0.4949 mm for (Cd-Zn)S films. For PC studies, coplanar electrodes (1.5 mm wide and 24 mm long at a separation of 6 mm) were formed by applying colloidal silver paint to the surface of the film. The photocurrents were measured exposing the total area of the film.

Measuring Instruments:
Citation source was an incandescent bulb of 100 W (power 18 mW) for PC rise–decay studies and of 1 kW excitation spectral studies. For recording the photocurrent, a nanometer (DNM-121) was used. For the optical absorption spectra, a Shimadzu (UV-VIS) Pharmaspec-1700 spectrophotometer was used.

RESULTS AND DISCUSSION

PC rise and decay studies:
PC rise and decay curves of different (Cd-Zn)S films are shown in fig.1. On varying the zinc content, no photocurrent was observed for 0.7 : 0.3 combination of CdS to ZnS under visible excitation. With increase in the volume of CdCl₄, the maximum current was recorded for 6 ml volume. Early, the content of H₂O₃ was also varied and the maximum photocurrent was observed for a volume of 5 ml.

The values of \( \frac{I_{p}}{l_{d}} \) ratio, trap depths, lifetime and mobility were evaluated by methods discussed in publications [4]. The values of \( l_{d}, l_{p}, \frac{I_{d}}{l_{p}} \), trap depths, lifetime and mobility for films prepared at various concentration of ZnS, were summarized in table 1. From the table, it is observed that the values of lifetime and mobility both increase in the presence of impurities, which may be a main cause of photo sensitization.

PC excitation spectra of different (Cd₀.₇-Zn₀.₃)S films are shown in fig.2. It was also observed that due to increasing concentration of ZnS, the peak positions of PC excitation spectra shifted towards shorter wavelength. A small change in peak positions and hence the corresponding band gaps are also seen. The correspondents and their comparison with the values obtained from optical absorption spectra are presented in table 2.

Optical Absorption Spectra

Optical absorption studies of different (Cd-Zn)S films show that with increase in concentration of ZnS, the band gap increases. On addition of CdCl₄, a slight change in the band gap is observed. The Optical Absorption spectra of (Cd-Zn)S: CdCl₄, Ho film is shown in fig. 3. It can be observed from the figure that, a broad peak in the region 450-510 nm is seen which is associated to the presence of Ho (shown by arrow). Ishizaka and Kurokawa have recently reported that, in the absorption spectra of Ho³⁺ doped Alumina films, a peak at about 450 nm was due to the transition \( ^{3}F_2 \rightarrow ^{3}G_{5/2} \) in Ho. In the presence of Ho, the band gap has been found to be 2.6 eV.

CONCLUSIONS

Reasonably good photosensitive materials can be prepared by a simple technique of chemical deposition of ZnS films. PC rise and decay studies show a photoconductivity gain of the order of 10⁶ on addition of
HITCON - 2007
16-17 March 2007

Inurity. The increased values of lifetime and mobility also indicate increased photo-responsivity. Optical absorption studies show the presence of Ho through the transition $Y, \rightarrow \ G$. Band gaps determined from optical absorption spectra and the PC excitation spectra are found to be almost similar.

ACKNOWLEDGMENT
One of the authors (SP) is grateful to Dr. Abraham Oommen, Executive Vice Chairman and Dr. R. N. Dixit, Director of M. P. Christian College of Engineering and Technology, Bhilai for kindly permitting to continue research work at Pt. R.S. U., Raipur.

REFERENCES

Table 1: Values of $I_{dp}, I_{pc}, \phi_{pc} / I_{dp}$, Lifetime ($\tau$), Mobility ($\mu$) and Trap depth ($E$) for different (Cd-Zn)S films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$I_{dp}$ (mA)</th>
<th>$I_{pc}$ (mA)</th>
<th>Gain $I_{pc} / I_{dp}$</th>
<th>Lifetime ($\tau$) (sec)</th>
<th>Mobility ($\mu$) (cm$^2$/Vsec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(Cd$<em>{0.9}$Zn$</em>{0.1}$)$_{0.05}$CdCl$_2$</td>
<td>0.15</td>
<td>90</td>
<td>$6 \times 10^3$</td>
<td>37.5</td>
</tr>
<tr>
<td>2</td>
<td>(Cd$<em>{0.9}$Zn$</em>{0.1}$)$_{0.05}$CdCl$_2$</td>
<td>0.1</td>
<td>124.2</td>
<td>$1.24 \times 10^3$</td>
<td>60</td>
</tr>
<tr>
<td>3</td>
<td>(Cd$<em>{0.9}$Zn$</em>{0.1}$)$_{0.05}$CdCl$_2$Ho</td>
<td>0.05</td>
<td>147.5</td>
<td>$2.9 \times 10^3$</td>
<td>73.5</td>
</tr>
</tbody>
</table>

DEPARTMENT OF APPLIED PHYSICS
Table 2: Values of bandgap energy determined from excitation spectra and absorption spectra for different (Cd, Zn)S films.

<table>
<thead>
<tr>
<th>S. No</th>
<th>Sample</th>
<th>Band gap energy (eV)</th>
<th>From excitation spectra</th>
<th>From absorption spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>(Cd$<em>{0.5}$-Zn$</em>{0.5}$)$_2$S</td>
<td>2.45</td>
<td>2.44</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>(Cd$<em>{0.7}$-Zn$</em>{0.3}$)$_2$S</td>
<td>2.48</td>
<td>2.47</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>(Cd$<em>{0.5}$-Zn$</em>{0.5}$)$_2$S</td>
<td>2.50</td>
<td>2.51</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>(Cd$<em>{0.5}$-Zn$</em>{0.5}$)$_2$: CdCl$_2$</td>
<td>2.48</td>
<td>2.45</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>(Cd$<em>{0.5}$-Zn$</em>{0.5}$)$_2$: CdCl$_2$, Ho</td>
<td>2.61</td>
<td>2.6</td>
<td></td>
</tr>
</tbody>
</table>
ST. THOMAS COLLEGE, BHILAI
NAAC ACCREDITED WITH B++ GRADE
DEPARTMENT OF ELECTRONICS & PHYSICS
NATIONAL SEMINAR ON "RECENT TRENDS IN ELECTRONIC MATERIALS & PHYSICAL SCIENCES"

Certificate

Certified that Ms. Sandhya Pillai from M.P.C.C.E.T., Bhilai has delivered a Talk / Presented a paper / participated in the National seminar which was held at St. Thomas College, Bhilai on 15th & 16th September 2006.

Topic:

[Signature]
Dr. Reny George
Principal & Chairman

[Signature]
Abhijeet Bardhan
Organizing Secretary
This is to certify that Mrs. SANDHYA PILLAI attended and actively participated in the short-term course on "Advanced Experimental Techniques", held at IIT Guwahati, Organised by the Department of Physics during 6th - 10th February, 2006.

(P. Agarwal) (R. Tiwari)
Course Coordinator QIP Coordinator