Effects of La Dopant on Nanocluster Size and Optical Band Gap of CdO Films Prepared by Sol–Gel Method

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The undoped and lanthanum doped cadmium oxide thin films were prepared by sol–gel method. The CdO films were doped with various percentages of La, 0.1, 0.5, 1, and 2 at.%. We have investigated the structural properties of the CdO films by atomic force microscopy. The obtained results show that both the grain size and the surface roughness of CdO films reduce with increase of La doping content. Additionally, the result shows a significant decrease of the transmittance in the range of 300 to 500 nm with increase of La doping level. The optical band gap of CdO films increases with La doped CdO films. It was found that the band gaps to be 2.25, 2.36, 2.4, 2.28, and 2.31 eV for La contents with 0.1, 0.5, 1, and 2 at.% doped CdO, respectively.

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1. Introduction

Cadmium oxide has received considerable attention because of its important properties. It is direct band gap energy with 2.2 eV [1]. Because of its high conductivity with high transparency in the visible region, it has been used in several applications including optoelectronic devices and photovoltaic applications [2–5]. Synthesis of CdO films with different types of doping elements such as Al [6, 7], Cu [8], Ga [9], F [10], Li–Ni [11], Bi [12], Fe [13], B–H [14] confirms the possibility of tuning their material properties to be utilized in new applications in optoelectronic devices and sensors.

Previous reports have showed that the effects of lanthanum doping on the dielectric, electrical and electromechanical properties on different material such as barium titanate [15, 16] and zirconium oxide [17]. Dakhel and Ali-Mohamed [18] have studied CdO films with lanthanum doping. They have prepared 1, 5, and 7% La doped CdO films by a spin coater sol–gel technique on amorphous glass and crystalline Si substrates. They have shown that La doping increases the CdO lattice parameter and the optical band gap energy decrease from 2.1 eV to 1.7 eV.

In this paper, we investigate both the structural and optical properties for undoped CdO and La-doped CdO film with various low percentages of La compared to that in Ref. [18]. Our aim is to improve new nanostructure CdO films to control their structural and optical properties to be utilized in new applications in optoelectronic devices.

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2. Experimental details

The undoped and lanthanum doped cadmium oxide thin films were prepared using the precursors: cadmium acetate dehydrate, lanthanum(III) acetate hydrate, methanol, and mono ethanolamine. Firstly, the cadmium acetate dehydrate (Cd(CH$_3$_COO)$_2$·2H$_2$O) (0.5 M) was dissolved in methanol for 30 min at 60°C and then, the monoethanolamine was added to this solution [11]. The CdO films were doped with various atomic percentages (0.1, 0.5, 1, and 2 at.%) of lanthanum. The La contents were calculated using atomic ratio formula and then, the CdO films were doped by the calculated atomic ratios of La. The solutions were stirred using a magnetic stirrer for about 30 min. The obtained sols were used for preparation of the CdO films. The films were grown on microscopy glasses using sol–gel spin coater at 1500 rpm for 30 s and then, the films were dried at 150°C for 10 min onto a hot plate to evaporate the solvent and remove organic residuals. The prepared CdO solid films were annealed at 400°C for 1 h in a furnace [11]. The surface morphology properties of the CdO films were performed using a PARK system XE 100E atomic force microscopy (AFM). The absorbance, transmittance and reflectance spectra of the films were measured using a Shimadzu UV-VIS-NIR 3600 spectrophotometer.

3. Results and discussion

The AFM images of pure CdO and La doped CdO films are shown in Fig. 1. The grain size and surface roughness values of the films are given in Table. It is observed that the particle size of CdO is decreased with increase in La-doping level. It can be seen in Fig. 1 that the surface roughness of the CdO film is changed with increase in La-doping level from 0 to 2%. It is evaluated...
that the surface roughness of the films depends on the
distribution of particles on surface of the films.

<table>
<thead>
<tr>
<th>Thin films</th>
<th>Grain size [nm]</th>
<th>$R_q$ [nm]</th>
<th>$E_g$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure CdO</td>
<td>350-250</td>
<td>174.65</td>
<td>2.25</td>
</tr>
<tr>
<td>0.1% La-CdO</td>
<td>250-200</td>
<td>107.70</td>
<td>2.36</td>
</tr>
<tr>
<td>0.5% La-CdO</td>
<td>150-105</td>
<td>120-58</td>
<td>2.40</td>
</tr>
<tr>
<td>1% La-CdO</td>
<td>130-80</td>
<td>207.16</td>
<td>2.28</td>
</tr>
<tr>
<td>2% La-CdO</td>
<td>80-55</td>
<td>90.43</td>
<td>2.31</td>
</tr>
</tbody>
</table>

The transmittance spectra of pure and La-doped CdO films are shown in Fig. 2. As seen in Fig. 3, the CdO films exhibit an absorption edge, and it changes with La doping.

The optical band gap of the CdO films is calculated using the expression [19]:

$$ (a\nu) = B(\nu - E_g)^n $$

where $B$ is constant, $a$ [m$^{-1}$] is the absorption coefficient, $\nu$ [Hz] is the photon frequency and $E_g$ [eV] is the optical band gap. The parameter $n$ specifies the allowed direct ($n = 1/2$) and indirect ($n = 2$) transition in the electronic band structure. The band gap $E_g$ was obtained from extrapolating the linear part of $(a\nu)^2$ vs. $\nu$ plot to $a = 0$ as shown in Fig. 4. It was found that the La doping concentration affects the energy band gap $E_g$. The direct band gap of pure CdO is 2.25 eV. This value is in good agreement with several reports [1]. The La doped CdO increases the band gap towards higher energy values which are in good agreement with the values reported by Dakhel and Ali-Mohamed [18]. The band gaps for CdO films were found to be 2.36, 2.4, 2.28, and 2.31 eV for La

in the wavelength range from 550 nm to 1000 nm region. Absorption spectra of pure and La doped CdO films are shown in Fig. 3. As seen in Fig. 3, the CdO films exhibit an absorption edge, and it changes with La doping.

The transmittance spectra of pure and La-doped CdO films were measured in the range of 200 to 1000 nm. Figure 2 shows that the La doping reduces the optical transmittance by up to 60% for 2% La doping CdO in the range of 300 to 450 nm. This observation is consistent with results reported in Ref. [18]. However, La doping improves the optical transmittance by up to 15% for 2% La doping
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with 0.1, 0.5, 1, and 2% doped CdO, respectively. The change in optical band gap with La doping is due to La$^{3+}$ ions incorporating into the crystalline structure. These ions occupy interstitial positions and in turn, a deformation is formed in the periodic crystal potential. The electrons are interacting with this potential and this interaction causes a change in the optical band gap.

The reflectance spectra of the undoped and La doped CdO films are shown in Fig. 5. It is observed that the average reflectance of CdO film is increased in the range of 200 to 500 nm and decreases from the range of 550 to 1000 nm with the increase in La doping level. The change in the reflectance of the films suggests that the refractive index of the CdO films is changed with La doping. The refractive index of the CdO film in the range of 550-1000 nm exhibits the lowest value for 2% La dopant, but the films exhibit the highest value for undoped CdO film. It is evaluated that the refractive index exhibits a normal dispersion behavior in 550-1000 nm range.

4. Conclusions

We have investigated the structural and optical properties of La doped CdO films with low concentration of La and synthesized by sol-gel method. The result of AFM studies for the surface of CdO films indicates that the crystal size of the CdO film can be modified by varying the La doping level. The films are formed from nanocluster consisting of nanoparticles. The size of nanocluster is controlled by La dopant. It was found that the band gap energy of CdO increase from 2.25 to 2.40 eV with the increase of La content up to 0.5% in the film.

Acknowledgments

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References