Structural and optical properties of CdO and CdO$_{0.99}$Cu$_{0.01}$ thin films prepared by pulsed laser deposition technique

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Abstract

Structural and optical properties of CdO and CdO$_{0.99}$Cu$_{0.01}$ thin films were prepared in this work. Cadmium Oxide (CdO) and CdO$_{0.99}$Cu$_{0.01}$ semiconducting films are deposited on glass substrates by using pulsed laser deposition method (PLD) using SHG with Q-switched Nd:YAG pulsed laser operation at 1064nm in 6x10$^{-2}$ mbar vacuum condition and frequency 6 Hz. CdO and CdO$_{0.99}$Cu$_{0.01}$ thin films annealed at 550 °C for 12 min. The crystalline structure was studied by X-ray diffraction (XRD) method and atomic force microscope (AFM). It shows that the films are polycrystalline. Optical properties of thin films were analyzed. The direct band gap energy of CdO and CdO$_{0.99}$Cu$_{0.01}$ thin films were determined from ($\alpha$hv)$^{1/2}$ vs. photon energy curve and found to be 2.3 eV for CdO thin film, comparing with that the CdO$_{0.99}$Cu$_{0.01}$film which found to be 2.2eV. The electrical measurements shows that the conductivity and mobility of the charge carriers increase when Cu doped CdO.

Key words

PLD, Cadmium Oxide, optical properties.

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Introduction

Cadmium (Cd) is a soft, ductile, silver-white metal that belongs together with zinc and mercury to group IIb in the Periodic Table. It has relatively low melting (320.9 °C) and boiling (765 °C) points and a relatively high vapour pressure. In the air cadmium is rapidly oxidized into cadmium oxide, cadmium oxide is used in batteries, electroplating...
baths, pigments, plastics, synthetic products[1].

Cadmium Oxide (CdO) attracts a great attention due to its electrical and optical properties. CdO is an n-type semiconductor with direct band gap at approximately 2.3eV. The wide band gap properties of semiconductors, like CdO, are of interest particularly for optoelectronic applications in transparent conducting oxides (TCO), solar cells, smart windows, optical communications, flat panel displays, photo-transistors, as well as other types of applications like IR heat mirror, gas sensors, low-emissive windows, thin film resistors, etc. [2-5].

There are several methods developed for the synthesis of CdO films such as spray pyrolysis [6,7], sputtering, chemical bath deposition(CBD), pulsed laser deposition, MOCVD, sol-gel spin coating method and thermal evaporation technique [8].

Pulsed laser deposition has become a widely used deposition technique for thin film growth. PLD presents several advantages with respect to other deposition techniques. In fact, due to the high energetic content of the ejected species, it allows low temperature deposition process. Moreover, its ability to congruently transfer the stoichiometry from the target to the films, allows the growth of complex materials. The technique is based on the vaporization process induced by focusing a high energy pulsed laser on the surface of the material. When the energy laser density is higher than a threshold value, which depends both on the material and the laser wavelength, a stream of atoms, molecules, and clusters is ejected from the target surface. Such a stream, known as a plume and being also composed of excited neutral and ionized species, emits radiation [9].

In this work pure CdO and Cu doped CdO films were deposited on glass and Silicon substrates by pulse laser deposition. The electrical, structure and optical properties were studied.

**Experimental procedure**

(0.01 wt %) Cu-doped CdO target for PLD was prepared by solid-state reaction method. The pulsed laser deposition experiment was carried out inside a locally designed vacuum chamber at pressure $(10^{-5}$ mbar) and ablated by a second harmonic generation (SHG) with Q-switched Nd:YAG pulsed laser operated at 1064nm. Pulse width 10nsec repetition frequency 6Hz and operated at 700mJ energy to generate plasma plume. Prior to deposition, glass substrates were cleaned in deionized water, and finally dried. In order to get a uniform film thickness, substrates were kept rotating during the deposition. The films were deposited on glass substrates with rate of deposition equal 0.5 nm/sec. All samples were annealed at 550 $^\circ$C to enhancement the structure of the samples. The thickness of the prepared film was measured by laser interferometer technique. The thickness of the film determined by this procedure is about 500nm. The structure of the film was obtained using X-ray diffraction (XRD) method (Shimadzo 6-2006, with Cu-K$\alpha$ radiation having wavelength $\lambda= 1.5406$ Å). Microstructure surface topography was examined using (AFM). Optical transmittance was recorded with a double beam Shimadzu UV-Visible spectrophotometer in the wavelength range 200-800 nm. The Hall measurement was determined by using HMS3000 Hall measurement setting.
Results and discussion

The XRD spectrum of CdO and CdO\(_{0.99}\)Cu\(_{0.01}\) films grown on the glass substrates are shown in Fig. 1. Three strong diffraction peaks are observed for planes (111), (200) and (220). The presence of different peaks in the figure shows that the films are polycrystalline in nature with preferential orientation along the (111) crystal plane. The results shown that the planes are enhanced in the CdO\(_{0.99}\)Cu\(_{0.01}\) films. The comparison of observed 2\(\theta\), d, I/I\(_0\) and (hkl) values for CdO and CdO\(_{0.99}\)Cu\(_{0.01}\) thin films are shown in Table 1.

There are no additional peaks without Cu upon doping indicates the solubility of the dopant in the crystal structure. This result is comparable with results obtained by [7, 10 and 11].

Table 1: Comparison of 2\(\theta\), d, I/I\(_0\) and (hkl) values for CdO and CdO\(_{0.99}\)Cu\(_{0.01}\) thin films.

<table>
<thead>
<tr>
<th>Peak no.</th>
<th>2(\theta) CdO</th>
<th>d spacing (10(^{-10})m) CdO</th>
<th>d spacing (10(^{-10})m) CdO(<em>{0.99})Cu(</em>{0.01})</th>
<th>I/I(_0) CdO</th>
<th>I/I(<em>0) CdO(</em>{0.99})Cu(_{0.01})</th>
<th>hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>33.4552</td>
<td>2.6763</td>
<td>2.70616</td>
<td>100</td>
<td>100</td>
<td>111</td>
</tr>
<tr>
<td>2</td>
<td>38.7497</td>
<td>2.3219</td>
<td>2.34405</td>
<td>81</td>
<td>80</td>
<td>200</td>
</tr>
<tr>
<td>3</td>
<td>55.7293</td>
<td>1.64811</td>
<td>1.65775</td>
<td>41</td>
<td>40</td>
<td>220</td>
</tr>
</tbody>
</table>

AFM images (2D and 3D) were prepared of the CdO and CdO\(_{0.99}\)Cu\(_{0.01}\) thin films on glass substrates as shown in Fig. 2a and b. Fig. 2a shows that Roughness average is about 4.31 nm and the Root Mean Square about 5.4nm while Fig. 2b shows that Roughness average is about 2.61nm and root mean square about 3.15nm. The grain analysis report which estimated for CdO and CdO\(_{0.99}\)Cu\(_{0.01}\) thin films and the average diameter of the particles about 98.65nm and 87.37nm are illustrated in Fig. 3a and b, respectively.
Fig. 2a, b: AFM images (2D and 3D) of CdO and CdO$_{0.99}$Cu$_{0.01}$ thin films.

Fig. 3a, b: AFM grain analysis report for the CdO and CdO$_{0.99}$Cu$_{0.01}$ thin films of 500 nm thickness.
The absorption spectrum of CdO and CdO\(_{0.99}\)Cu\(_{0.01}\) thin films with thickness 500nm is shown in Fig.4. The figure shows high absorption coefficient in the UV region, whereas it is transparent in the visible region for CdO film, and it is increasing and shifted toward the visible region for CdO\(_{0.99}\)Cu\(_{0.01}\) film.

![Absorption spectrum of CdO and CdO\(_{0.99}\)Cu\(_{0.01}\) thin films.](image)

**Fig.4: Absorptance spectrum of CdO and CdO\(_{0.99}\)Cu\(_{0.01}\) thin films.**

Fig.5 estimated the optical transmittance spectra with wavelength from (400-750nm) of the CdO and CdO\(_{0.99}\)Cu\(_{0.01}\) thin films. It is observed from this figure that the films show high transmission in the visible region and low transmission in the UV region. The optical transmittance increases for CdO\(_{0.99}\)Cu\(_{0.01}\) film.

![Transmittance spectrum of CdO and CdO\(_{0.99}\)Cu\(_{0.01}\) thin films.](image)

**Fig. 5: Transmittance spectrum of CdO and CdO\(_{0.99}\)Cu\(_{0.01}\) thin films.**

The reflectance (R) has been found by using the relationship:

\[ R + T + A = 1 \]  

where (A) is the absorption and (T) is the transmission. Fig.6 shows the reflectance spectra for the CdO and CdO\(_{0.99}\)Cu\(_{0.01}\) thin films as a function of wavelength. It is clear from this figure that the reflectance of the films increased with the increasing of the wavelength for CdO\(_{0.99}\)Cu\(_{0.01}\) thin film, while decreased for CdO thin film at wavelength in the range 590-750 nm.
Assuming direct transition, the dependence of \((\alpha h \nu)^2\) on the photon energy \((h \nu)\) is plotted following Tauc relation\[11,12\] and the graph is illustrated in Fig. 7. The extrapolation of the linear part of the above plot to \((\alpha h \nu)^2=0\) gives the energy gap values of the CdO and CdO\(_{0.99}\)Cu\(_{0.01}\) films, which were found to be about 2.3eV and 2.2eV respectively. It can be noticed from this figure that the value of energy gap is decreasing for CdO\(_{0.99}\)Cu\(_{0.01}\) film. These values are in a good agreement with the values presented by other workers\[13\].

The refractive index \((n)\) is an important parameter for optical materials and applications. Thus, it is important to determine optical constants of the films. The refractive index of the films was determined from the following relation\[14\]:

\[
n = (\frac{1+R}{1-R}) + \frac{4R}{(1-R)^2} - k^2
\]  

where \(k\) is the extinction coefficient \((k=\alpha \lambda /4\pi)\). Fig. 8 shows the variation of the refractive index as a function of the wavelength for both CdO and CdO\(_{0.99}\)Cu\(_{0.01}\) thin films, which indicate that the refractive index increases with increasing of wavelength for CdO\(_{0.99}\)Cu\(_{0.01}\) thin film, because the refractive index is a function of wavelength, while decreased for CdO thin film at wavelength in the range 580-750 nm.
The relation between the extinction coefficient ($k$) and wavelength for CdO and CdO$_{0.99}$Cu$_{0.01}$ films deposited are shown in Fig. 9. From this figure we can observe that $k$ values of CdO$_{0.99}$Cu$_{0.01}$ film larger than $k$ values of CdO film and take high values in the UV region, whereas it is decreasing in the visible region for CdO and CdO$_{0.99}$Cu$_{0.01}$ thin films.

The dielectric constant is defined as $\varepsilon(\omega) = \varepsilon_r(\omega) + i\varepsilon_i(\omega)$, real and imaginary parts of the dielectric constant are related to the $n$ and $k$ values. The $\varepsilon_r$ and $\varepsilon_i$ values were calculated using the formulas [15]:

$$\varepsilon_r = n^2 - k^2$$  (3)

$$\varepsilon_i = 2nk$$  (3)

The variation of the real ($\varepsilon_r$) and imaginary ($\varepsilon_i$) parts of the dielectric constant values versus wavelength in the range 400-750 nm are shown in Fig. 10 a and b.
From Fig. 10a it is clear that the real part of the dielectric constant for CdO$_{0.99}$Cu$_{0.01}$ thin film increase as the wavelength increase, while decreased for CdO thin film at wavelength in the range 590-750 nm. Also the variation of (\(\varepsilon_r\)) has similar trend to the variation of the refractive index because of the smaller values of k$^2$ in comparison with n$^2$ and the values of real part are higher than imaginary part. Fig. 10b shows the imaginary part of the dielectric constant for CdO and CdO$_{0.99}$Cu$_{0.01}$ thin films. The variation of the (\(\varepsilon_i\)) mainly depends on the variation of k values which related to the variation of absorption coefficient. The imaginary part of dielectric constant for CdO thin film increase with wavelength but when reach 580 nm \(\varepsilon_i\) become decreases with increase the wavelength, while for CdO$_{0.99}$Cu$_{0.01}$ thin film this constant increasing with wavelength.

The Hall measurements show that the CdO and CdO$_{0.99}$Cu$_{0.01}$ films deposited on glass substrate are n-type semiconductor, the observed characteristics were supported from the measurements of mobility, conductivity, resistivity and Hall coefficient as illustrated in Table 2).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CdO</th>
<th>CdO$<em>{0.99}$Cu$</em>{0.01}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk concentration (1/cm$^3$)</td>
<td>-2.208E+19</td>
<td>-5.202E+19</td>
</tr>
<tr>
<td>Mobility (cm$^2$/V.s)</td>
<td>3.995E+1</td>
<td>9.233E+1</td>
</tr>
<tr>
<td>Resistivity ((\Omega).cm)</td>
<td>7.076E-3</td>
<td>1.300E-3</td>
</tr>
<tr>
<td>Conductivity (1/(\Omega).cm)</td>
<td>1.413E+2</td>
<td>7.6965E+2</td>
</tr>
</tbody>
</table>

The result shows the mobility and conductivity increase in CdO$_{0.99}$Cu$_{0.01}$thin films, where the resistivity decreases.

**Conclusion**

The CdO and CdO$_{0.99}$Cu$_{0.01}$ thin films prepared by pulse laser deposition technique were deposited on glass substrates. The thickness of the films was 500nm. The structure analysis shows that the films are polycrystalline structure. From UV-Visible transmittance, absorbance spectra, it observed that the optical transition in the CdO and
CdO$_{0.99}$Cu$_{0.01}$ films to be direct transition. The energy band gap for CdO and CdO$_{0.99}$Cu$_{0.01}$ equals to 2.3eV and 2.2eV; respectively. The Hall measurements result show the films are n-type semiconductor and the mobility increase in CdO$_{0.99}$Cu$_{0.01}$ films, while the resistivity decreases.

References