Effect of Manganese Contain on the Optical Properties of CuO Thin Films

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Abstract Copper oxide prepared with various contains of Manganese by chemical spray pyrolysis. Some optical properties are studied from recording the absorption spectra via UV-Visible spectrophotometer in the range of 460-900 nm. The absorbance increased with increasing Mn-contain in the CuO thin films, and the absorption coefficient. Extinction coefficient and refractive index are decreased with increasing Mn-contain in the CuO thin films, also the energy gap shifted from 2 eV to 1.91 eV after 4%Mn additive.

Introduction

Copper Oxide has been studied as a semiconductor material because of natural abundance of starting material (Cu); low cost production processing; non-toxic nature and reasonably good electrical and optical properties [1]. Copper forms two well-known oxides, tenorite (CuO) and cuprite (Cu_2O). Both the tenorite and cuprite were p-type semiconductors having band gap energy of 1.21 to 1.51 eV and 2.10 to 2.60 eV respectively [2,3]. CuO absorbs strongly throughout the visible spectrum and is black in appearance [4].

Copper oxide films have been deposited using several techniques such as oxidation of copper sheets [5], electrodeposition [6], ultrasonic spray pyrolysis [7], reactive sputtering [8], and chemical path deposition [9]. Ferromagnetism has been observed in 15.2%–29.8% Mn doped CuO thin film with a transition temperature between 87.0 and 91.5 K [10].

The optical properties of CuO thin films prepared by chemical spray pyrolysis method and effect of Mn contain of these films are studied.

Experimental Part

In present work, 0.1M of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (supplied from Sigma-Aldrich Chemicals) and 0.1M of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (supplied from Merck Chemicals) were used as precursor materials dissolve in double distilled water to growth CuO:Mn films by chemical spray pyrolysis on glass substrate. Some parameters and conditions that used to preparation these films such as: Substrate temperature was kept at 400°C, the distance between nozzle and substrate was 30 cm, the carrier gas was compressed air, and deposition rate was 5 ml/min. Weighting method was used to determine the films thickness (300 nm). UV-Visible spectrophotometer used to record absorbance spectra and determine some physical properties.

Results and Discussion:

The UV-VIS absorption spectra of CuO and Mn-doped CuO thin films prepared by chemical spray pyrolysis method in the range of 460-900 nm are presented. Fig.1. represents the relationship between absorbance spectra and wavelength. From this figure, it can be noticed the increases of absorbance with increasing Mn-doping in the all prepared CuO:Mn thin films. This behavior attributed to the formation of sub-levels in the energy gap with the addition of Mn particles.

Fig.1: Optical absorbance spectra of CuO:Mn thin films.

The absorption coefficient (α) could be calculated by using the following relation [11]:

$$\alpha = \frac{2.303A}{t} \quad (1)$$

Where (A) is the absorbance and (t) is the film thickness. Fig. 2 represent the relationship between the absorption coefficient and the photon energy ($h\nu$). The absorption coefficient increased with increasing photon energy and with increases of Mn-content in the CuO thin film. The values of $\alpha > 10^4$ for all films that refer to the direct transition of these films.

Fig.2: Absorption coefficient of CuO:Mn thin films.

The extinction coefficient (k) which is represented the extinction of electromagnetic wave in material is calculated from the following formula:

$$k = \alpha\lambda/4\pi \quad (2)$$

where (α) is the absorption coefficient and (λ) is the wavelength. The extinction coefficient decreased with increasing Mn content in the CuO thin films for all prepared thin films as shown in Fig. 3.

Fig.3: Extinction coefficient of CuO:Mn thin films.

The refractive index (n) is a fundamental optical property of thin film that is directly related to other optical properties. The refractive index (n_o) of pure and doped CuO thin film with Mn was determined from the relation [12]:

$$n_o = \left(\frac{1+R}{1-R} \right) + \sqrt{\frac{4R}{(1-R)^2} - K_o^2} \quad (3)$$

Where (R) is the reflectance and (k) is the extinction coefficient. The variation of refractive index with wavelength of CuO thin films with various concentration of Mn are presented in Fig. 4. The refractive index decreased with increasing of Mn content until wavelength of 650 nm, and then take another behavior at wavelengths greater than 650 nm.

Fig.4: Refractive index of CuO:Mn thin films.

The direct optical band gap E_g of the films is obtained from the transmission spectra by using the following relationships:

$$(\alpha h\nu)^2 = B (h\nu - E_g) \quad (4)$$

Where: (α) absorption coefficient, (h) Planck's constant, (ν) the frequency of the photon, ($h\nu$) photon energy, (B) constant depends on the probability of the transfer of electrons.

The Figs. 5-8 reveal that the extrapolation of the linear portion of the graph to energy axis at $(\alpha h\nu)^2 = 0$ produce the E_g value. From these figures, the energy gap decreased with increasing Mn-doping in the CuO:Mn thin films from 2 eV for pure film to 1.91 eV for 4% Mn addition in the films. This behavior attributed to the formation of sub-levels in the energy gap of prepared films.

Fig.5: Variation of $(\alpha h\nu)^2$ as a function of photon energy of CuO thin films.

Fig.6: Variation of $(\alpha h\nu)^2$ as a function of photon energy of CuO:2%Mn thin films.

Fig.7: Variation of $(\alpha h\nu)^2$ as a function of photon energy of CuO:4%Mn thin films.

Fig.8: Variation of $(\alpha h\nu)^2$ as a function of photon energy of CuO:6%Mn thin films.

Conclusions

Copper oxide growth by chemical spray pyrolysis. Some optical properties are studied from recording the absorption spectra in the range of 460-900 nm. The absorbance absorption coefficient α increased with increasing Mn-content in the CuO thin films, while extinction coefficient and refractive index are decreased with increasing Mn-content in the CuO thin films. The energy gap shifted from 2 eV to 1.91 eV after 4%Mn additive in CuO thin films.

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