Studying the effect of annealing temperatures on the optical properties of CdS:1% Cu nanoparticles thin films prepared by thermal evaporation technique

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Abstract. In the present study, thermal evaporation technique in vacuum has been used to prepare CdS thin films doped with 1% Cu nanoparticles with average particles sizes 50 nm. The effect of annealing temperatures with different ranges (R.T, 250, 300 and 350 °C) on the structural and the optical properties of the prepared thin films were studied. The XRD technique has been used to study the structural properties of the prepared thin films. The AFM analysis shows that the increase in the (RMS) leads to decrease in the roughness values by increasing of the annealing temperature. The optical measurements showed that the CdS: 1% Cu films have direct optical energies gaps (Eg), and it decreases from 2.43 eV to 2.39 eV with the increasing of annealing temperatures (R.T – 350) °C. The optical properties had measured in the range (200-800) nm of wavelength. The refractive index (n), extinction coefficient (k), absorption coefficient (α) and the real and imaginary dielectrics constants (ε_r and ε_i) increased by increasing the annealing temperature.

Keywords: Thin films, Annealing temperature, Structural properties, Optical properties, CdS:1%Cu, nanoparticles.

1. Introduction

Cadmiums Sulfides (CdS) is one of the greatest studied mixes with a direct bands gaps of about (2.45eV) [1] which using widely in many requests, counting solar cells [2], photos transistor [3], and diode [4] transparent electrode [5], gases sensor [6]. Cadmiums Sulfides film set by numerous ways, like thermal-evaporation, spray-pyrolysis, chemical-bath depositions, gradients recrystallizations and growths, spins-coating, pulsed lasers depositions, closed spaced sublimations [7] and sprays pyrolysis depositions (SPD) [8] using in the depositions of CdS thins films. Thin films of Cds:Cu were synthesized. The paper aimed to study the effects of annealing temperature on the structural and optical properties of Cadmiums Sulfides doping with Coppers films deposited by thermal evaporation methods.

2. Experimental Work

The CdS: 1%Cu thin films arranged by thermal evaporation techniques. The specifics weights of Cadmiums Sulfides powders (99 wt. %) reserved and placed in a molybdenum boats, by taking (1wt. %) from Copper weight and placed it in other molybdenum boats. the rates of evaporations nearly equal to 4.1A/sec and the films thickness in the ranges of 300 nm measuring by interferences methods, the substrates glasses placing directly above the sources at a distance of nearly about 16 cm after cleaning the glasses.

The arranged thins films annealed at different annealing temperatures (R.T, 250, 300 and 350 °C) for 2 hours. The optical constants absorptions coefficients (α), extinctions coefficients (k) and reals (ε_r) and imaginary parts (ε_i) of dielectrics constants calculated from the following equations [8].

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

Where t is the films thicknesses and A is the optical absorbance.

$$K = \frac{\alpha \lambda}{4\pi}$$  \hspace{1cm} (2)

Where λ: is the wavelengths of the incidents rays.
\[ e_r = n^2 - k^2 \]  
\[ e_r = 2n \kappa \]

Where \( n \) is the refractive index obtained from the following relations [9].

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

### 3. Results and Discussions

Figure (1) shows the XRD spectra obtained at different annealing temperatures for CdS:1%Cu films. The XRD patterns for Cadmium Sulfides doped with Coppes films at different annealing temperatures (RT, 250, 300 and 350 °C) shows that all peaks in the patterns correspond to hexagonal structures of CdS. No changes in the characteristics peaks positions observed in samples doping with Cu. Which explain that the doped CdS samples retains the hexagonally structures. Observing that there is changing in the heights and broadenings of the peaks could recognize to the change in the scattering factors corresponding to incorporated elements. The incorporations of Cu\(^{2+}\) ions do not change the crystals structures of the CdS films. The increasing of peaks intensity of (002) planes with respect of (010) planes with increasing of dopant concentrations this behavior was observed by others researchers [10, 11, 12].

Which meaning the c-axis of CdS films changes from inclined to the substrates to perpendicular to substrates. The average (101) interplaner distances \( d \) (101) calculating using the formula [6].

\[ n \lambda = 2d \sin \theta \]  

The spacing of the d (101) lattices planes decreases with increases Cu/Cd ratios, since the ionic radius of Cu\(^{2+}\) (0.96 Å) is smaller than Cd\(^{2+}\) (1.03 Å) [13], this suggests that Cu\(^{2+}\) ions replaces the Cd\(^{2+}\) ions in the lattices substitutional. Mean some of the Cu\(^{2+}\) ions enter the lattices interstitially but the d value continues to decrease as the Cu concentrations increases ratios increases, probable that the majority of Cu\(^{2+}\) ions are replacing Cd\(^{2+}\) ions substitutional, this is observed by other workers [13, 14].

Fig. (2) Shows the morphological CdS: 1% Cu nanoparticles thin films deposited on glasses substrates with different annealing temperatures (R.T, 250, 300 and 350 °C) for 2 hours. These images show the comparatively uniforms, dense and strips like structures grains distributions over the substrate. The values of average grains sizes increased with increasing the annealing temperatures. While the roughness values obtaining decreasing with the increasing of the annealing temperatures. The surfaces of the samples relatively smaller roughness’s values at (350 °C), higher annealing temperatures may lead to a slight annealing effects, which results in the smoother surface compared to films deposited at 250 °C. The peaks look sharper by decreasing the substrate temperature as the average grain size decreases. Temperature enhance the quality of the film. These values are which agreed with the values reported by other researchers [7, 9].

Fig. (3) Shows the energy gaps as a function of photons energy of CdS: 1% Cu nanoparticles for different annealing temperatures, from the figures and tables (1) the energy gaps decreased as the annealing temperatures increased. The direct bands gap values were calculated as (2.44, 2.42, 2.41 and 2.39) eV at different annealing temperatures of (R.T, 250, 300 and 350 °C) respectively. This caused by the increases of the density of localized states in the \( E_g \), which causes a shift to lower values. This result agrees approximately with the result reported by Iqbal et al. [7].

Fig. (4) Shows the optical transmittances spectra as a function of wavelengths of incident lights on CdS:1% Cu nanoparticles for different annealing temperatures. The films have transmittances at the ranges of wavelengths (200-800) nm with a gradual falls nears the fundamentals absorptions regions. The transmittances of thins films increased with increasing the annealing temperatures. This increasing of transmittances with increasing substrates temperatures due to variations in the imperfections and the inner strains and the CdS thin films properties of crystallite, these results agree with Abbas [15].

Figure (5) Shows the variations in refractive index as a functions of incidents wavelengths on CdS 1% Cu nanoparticles for different annealing temperatures. Clearly, the refractive index increase with increasing of the annealing temperatures, this could be returns to heat treatment effects on the environment of films surfaces in which the reflections could occur and that would make a variation in refractive index [12].
Fig. (6) Shows the extinction coefficients as a functions of incidents wavelengths lights on CdS:1% Cu nanoparticles for different annealing temperatures. The extinction coefficients \( k \) increases with the increasing of annealing temperatures of films, which is indicates that Cu\(^{+2} \) ions will changes the structures by interstitially positions among the CdS atoms from increasing the annealing temperatures [13].

Fig. (7) and (8) represents the reals \( (\varepsilon_r) \) and imaginary dielectrics constants \( (\varepsilon_i) \) as a functions of incidents wavelengths lights on CdS:1% Cu nanoparticles for different annealing temperatures.

The real parts increase with the annealing temperatures raising, and this indorsed to the same reason mentioned previously for the refractive index, also imaginary part increases with the increases of annealing temperatures and this is due to the similar interpretations discussed previously for the extinction coefficients. The real part relates to dispersions, while the imaginary part provides a measures to dissipative rate of the waves in the mediums [14].

**Table 1.** Illustrate the grain size, roughness, RMS and Eg of CdS 1% Cu nanoparticles for different annealing temperatures

| CdS:1% Cu Annealing Temp. \(^{0}\)C | Grain size \( \text{(nm)} \) | Eg \( \text{(eV)} \) | Roughness \( \text{(nm)} \) | RMS \( \text{(nm)} \) |
|-----------------------------------|-----------------|-------------|----------------|----------------|
| R.T                               | 17.8            | 2.43        | 36.858         | 29.7           |
| 250                               | 17.5            | 2.42        | 15.102         | 30.4           |
| 300                               | 17.1            | 2.41        | 12.921         | 32.5           |
| 350                               | 16.7            | 2.39        | 10.531         | 36.0           |

**Figure 1.** X-ray diffraction patterns of CdS: 1% Cu nanoparticles for different annealing temperatures
Figure 2. AFM images for CdS 1% Cu nanoparticles for different annealing temperatures

Figure 3. The energy gap as a function of photon energy of CdS:1%Cu nanoparticles for different annealing temperatures
Figure 4. Transmittance spectrum as a function of wavelength of incident light on CdS:1%Cu nanoparticles for different annealing temperatures

Figure 5. The refractive index as a function of incident wavelength light on CdS: 1% Cu nanoparticles for different annealing temperatures

Figure 6. The extinction coefficient as a function of incident wavelength light on CdS: 1% Cu nanoparticles for different annealing temperatures
4. Conclusion
The effect of annealing temperature on the structures and optical properties of CdS:1%Cu thin films deposited by using thermal evaporation technique were conducted. The structural properties for the prepared films were studied by X-Ray diffractions and it appeared that the films are polycrystalline and have hexagonal structures, with a preferred orientation along (002). The atomic force microscopy (AFM) showed an increasing in (RMS) and a decreasing in roughness values with increasing of annealing temperatures degrees. The films show a direct optical energy gaps ($E_g$), and it decreases with the increasing of annealing temperatures. All films exhibit high transmittance. The transmittance spectra, extinctions coefficients, the refractive index, dielectric constants real parts ($\varepsilon_r$) and imaginary part $\varepsilon_i$ show an increasing when the annealing temperature were increased.
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