Structure and Optical Properties of CdSe:Ga Thin Films Prepared by Thermal Evaporation Method

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Abstract

Cadmium Selenide (CdSe and CdSe:Ga) alloy has been prepared successfully in an evacuated quartz tube at a pressure (10⁻² Torr). The structure of the CdSe alloy (powder) was tested by X-ray diffraction (XRD) and found as a polycrystalline (hexagonal) structure. CdSe and CdSe: Thin films have been deposited with a thermal evaporation process on the glass and Si substrates. The aim of this kind of study was to determine the ultrastructural morphology and optical properties of pure CdSe and Ga doped films produced using a method of thermal evaporation. The effect of Gallium on the structural and optical properties of CdSe thin film were doped at 0, 1, 3 and 5%. For all Ga doping ratios, the structural features such as the size of the grain and the micro strain of the thin film have been clarified with XRD technique and XRD pattern. The chosen orientation (002) for all prepared film has been polycrystal structures (hexagonals). With an increase in Ga from 37.54 to 21.37 nm, the grain volume decreases. AFM and SEM were used to study the morphology and surface roughness of the CdSe pure and doping films. All films were homogeneous with a characteristic spherical grain size depending on Ga concentration. The roughness of the films increases with the increase of Ga dopant. UV-Visible spectra photometer is used to investigate the visible properties such as absorption, absorption coefficient and energy gaps in thin films. The absorption value subsequently increased with Al doping concentration of localized states in the band gap of the films increases with the increasing of Al dopant, where optical energy gap values decreased with increasing the proportion of the doping in the range between 1.74 and 1.62. The grain size for pure and Ga- doped CdSe of thin films were decreased with Ga ratios. The absorption coefficient determined depends on photon energy incident (hv), the energy gap of the semiconductor as well as the form of transitions. In conclusions, CdSe and CdSe:Ga were successfully prepared from pure elements Cd, Se and Ga. XRD patterns showed the CdSe and CdSe:Ga films are polycrystalline of hexagonal structure directions by Ga doping that orientated a peak became less intensity from undoped CdSe film. The XRD patterns and AFM measurements of Ga-doped and undoped CdSe thin films agree with each other of the grain size within nanocrystal range and decrease as Ga doping concentration increases. AFM images indicate that the increasing in Ga doping that showed smooth surface films compared to the CdSe films. The optical bands gaps of the films have a direct band transition and slightly decreased with the increasing Ga doping.

Keyword: CdSe, Ga, Thin films, XRD, AFM, Optical properties.

1. Introduction: Due to their large absorption coefficients, the optical band gap 1.74 eV at room temperature and high photosensitivity, cadmium selenide (CdSe) is a promising material for the thin films with the compound II-VI semiconductors. [1, 2]. Usually, CdSe is a n-type material which has an interested for their applications as photoconductors [3], solar cells [4,5], thin film transistors [6,7], gas sensors [8,9]. The preparation of CdSe thin films there are different methods have been used such as pulsed laser deposition technique [10], thermal evaporation technique [11], spray deposition [12], electrodeposition [13], chemical bath deposition [14], molecular beam epitaxy (MBE) [15]. A higher
energy band gap ternary doped with other metals was demonstrated by several researchers for the increased short circuit current in solar cells[16]. Research was also carried out on the enhanced properties of CdSe doped with thin film [17], Cu [18], Al [19], Fe [20], Hg [21] and Sn [22]. By using different elements, the effects of doping on CdSe films prepared by different methods have been studied extensively. However, doping effect studies on CdSe by thermal evaporation technique at room temperature on glass substrate are very limited. The objective of this study was to determine the ultrastructural morphology and optical properties of both pure CdSe and Ga doped films prepared by thermal evaporation method have been reported

2. Experimental Procedure: Four Samples of CdSe and CdSe: Ga were prepared by direct mixing of Cd and Se highly purified, with a direct atomic ratio in 0, 1, 3, 5% alloy, as defined on table (1), with 10-2 torr at the base pressure reserved in evacuated quartz ampoules. The light bulbs were held in the oven at 12000 C at the constant heating rate of 5 0 C / min. for a period of five hours. The ampoule was continuously rocked during the heating process to achieve the homogeneous blend of the alloys. Thin films of the prepared alloys were made by evaporation technique in pressure about 2.3 × 10^5 torr before that cleaned glass slides were used as the substrates. The distance between the source of molybdenum boat and substrate was approximately 9 cm. The flow rate has been maintained at 7.8 A0 /s, and thin films of samples used were prepared with thickness of 400±20nm.

| Ratio of Cadmium | Ratio of Selenide | Ratio of Gallium |
|------------------|------------------|-----------------|
| 58.66%           | 41.34            | 0%              |
| 58.66%           | 40.34            | 1%              |
| 58.66%           | 38.34            | 3%              |
| 58.66%           | 36.34            | 5%              |

3. Results and Discussion:

3.1 Structural Properties

a) X-ray Diffraction: The prepared powder was tested by X-ray diffraction and according to the (ASTM) card it is prove powder that is CdSe as illustrated in the table (2) and shown in (Fig. 1). The deposited CdSe:Ga films were characterized by the X-ray wavelength diffraction Cukuα for the purposes of the investigation of structural properties (1.54 nm). Fig. 1 shows 0, 1, 3 and 5% pure XRD pattern of CdSe thin movies doped with the Gallium. These patterns show the polycrystalline nature of these films with a root structure (hexagonal) with preference for (002) and a small peak (1103) plane. Furthermore, the gallium cannot break the CdSe matrix structure in a way that maintains the hexagonal structure. Fig. 2, shows a peak in diffraction with increasing Ga content in CdSe shifting in the blue shift pattern. The substitution of smaller Ionic radii of Gallium atoms 0.062 nm by broad Ionic Cadmium 0.097 nm
indicates a minor improvement in the approximate interplaner gap. It can calculate the distance between the levels of the diffraction angles at a certain peak by using (Bragg's law) [22],

\[ n\lambda = 2dsin\theta \]  

(1)

\( n \): Integer number which represents the degree of interference (n=1,2,3), (n=1.54Å), (d) is the distance between the diffracting planes. The particle size (D) for CdSe and CdSe:Ga thin film samples were calculated corresponding the most intense diffraction peak of (002) using Scherrer’s formula [22]:

\( \lambda \): The wavelength of the X-ray, \( \beta \) : Full width at half maximum (FWHM), \( \theta \): Is the Bragg's angle.

| (hkl) (ASTM) | 2θ(deg) (ASTM) | 2θ(deg) observed | (ASTM) d(Å) | d(Å) Observed |
|--------------|----------------|-----------------|-------------|---------------|
| 100)         | 23.901         | 23.7136         | 3.720000    | 3.74903       |
| 002)         | 25.354         | 25.4855         | 3.510000    | 3.49225       |
| 101)         | 27.080         | 27.2074         | 3.290000    | 3.27502       |
| 102)         | 35.107         | 35.2726         | 2.554000    | 2.54246       |
| (110)        | 41.968         | 42.0907         | 2.151000    | 2.14504       |
| 103)         | 45.788         | 45.9015         | 1.980000    | 1.97543       |
| 200)         | 48.845         | 48.9840         | 1.863000    | 1.85809       |
| (112)        | 49.669         | 49.8153         | 1.834000    | 1.82901       |
| 201)         | 50.673         | 50.8178         | 1.800000    | 1.79526       |
| (202)        | 55.842         | 55.9770         | 1.645000    | 1.64140       |
| (203)        | 63.881         | 63.9680         | 1.456000    | 1.45427       |
| (210)        | 66.386         | 66.4473         | 1.407000    | 1.40589       |
| (211)        | 67.859         | 67.9835         | 1.380000    | 1.37782       |
| (105)        | 71.904         | 72.0180         | 1.312000    | 1.31023       |
| (212)        | 72.292         | 72.4206         | 1.305900    | 1.30052       |
| (300)        | 76.726         | 76.8049         | 1.241100    | 1.24006       |
| (213)        | 79.430         | 79.5413         | 1.205500    | 1.20413       |

**Table 2**: Comparing the results of X-ray diffraction pattern of the Cadmium selenide material prepared with that of the (ASTM) card.
Fig. 1: X-ray diffraction pattern of CdSe powder.

Fig. 2: X-ray diffraction pattern of CdSe and CdSe:Ga thin films.

Calculated pure and Ga-doped grain sizes at 0, 1, 3, 5% CdSe are shown in the table (3). The grain size was reduced by doping of Ga. It is observed. The reason was its smaller size of Ga$^+$ ion compared to Cd$^-$ ion, which contributes to a decrease in the grain size and an increase in doping concentration (Fig. 3). These grain size values have been matched by [23]. The relationship was determined for the microstrands of the thin films [21].
Table 3: Includes X-ray diffraction results.

| Ga% | 2θ degree | d_{hkl} (Å) | FWHM | Grain size (nm) | Micro strains *10^{-3} |
|-----|-----------|-------------|------|----------------|-------------------------|
| 0   | 25.4159   | 3.50166     | 0.2157 | 37.5448        | 52.6053                |
| 1   | 25.4495   | 3.49711     | 0.2250 | 35.9906        | 54.8698                |
| 3   | 25.4300   | 3.49975     | 0.2360 | 34.3144        | 57.5546                |
| 5   | 25.4396   | 3.49845     | 0.3789 | 21.3725        | 92.4026                |

Fig. 3: shows of grain size and dislocation as a function of doped percentage.

b) Atomic Force Microscopic Results: From AFM results shown in figure (4), it can be noticed that the increase in dopant percentage results lead to decrease in grain size and this in agreement with XRD measurement of particle size. Furthermore, the difference between particle size values which obtained from sharer’s equation (2) in XRD data and that obtained from the AFM measurements can be noticed. The reason behind that back to AFM is measuring the sample surface only without taking into consideration the structural defects as opposed to take these defects when calculating particle size by XRD [24].

Table 4: The grain size, roughness average and root mean square of thin film for CdSe and CdSe:Ga.

| Thin films and dopant% | Grain size, (G.S)(nm) | RMS Roughness (nm) |
|------------------------|-----------------------|--------------------|
| CdSe pure              | 99.92                 | 0.574              |
| CdSe:1%Ga              | 95.03                 | 1.26               |
| CdSe:3%Ga              | 93.78                 | 1.71               |
| CdSe:5%Ga              | 87.81                 | 1.94               |
Fig. 4: show the AFM of thin film for CdSe and CdSe:Ga with different dopant percentage (a) pure (b) 1% (c) 3% (d) 5%.

c) Field Emission Scanning Electron Microscope (FESEM): The structural analysis of samples was discovered by FE-SEM. The SEM images of CdSe and CdSe:Ga with concentration of 0, 1, 3 and 5%
thin films prepared using thermal evaporation method at R.T are showing in Figs.5 respectively. The morphological characteristics of thin films have been analyzed and have been observed SEM photographs of the samples. In Fig. 5a), the SEM for pure shows the agglomerates of particle are irregular shape. It demonstrates clearly the formation of spherical nanoparticles. It has been noticed that particles tend to spherical on the surface and form agglomerates that shown in Figs. 5a, c, d). In the same time, it is could distinguish that the particles images are not only spherical, see Fig. 5-b) but showed nanoparticles vary in shape (nanorods).

Figs. 5 (a, b ,c and d): FE-SEM images of CdSe and CdSe:Ga thin films with different dopant percentage.
3.2 Optical Properties: Using the UV–VIS spectrophotometer at room temperature to record the optical transmission spectrum from 300 to 1,100 nm wavelength. The absorption of the substratum is corrected by inserting in the reference beam an uncoated cleaned glasser layer. The relation can be used for measurement of the absorption coefficient $\alpha$ [25].

$$\alpha = \frac{2.303 (A - A')}{d} \tag{4}$$

Where: $A$: is the absorption at a certain wavelength, $A'$: is the correction factor, $d$: is the thickness of film

a) Absorption: Spectra absorption of the doped CdSe films were increased with increasing of the doped ratio of Gallium in order to get absorption processes by doping levels resulting from gallium which increases the absorbance. These processes are accompanied with a shift of the sharp edges (absorbance edge) towards the low energies with increasing of the doping of 0, 1, 3, 5% (Fig 6).

![Fig 6: Optical absorbance of CdSe and CdSe:Ga with different dopant percentage.](image)

b) The Absorption Coefficient: The coefficient of absorption $\alpha$ was calculated from the high absorption area on the film's fundamental absorption edge. Different volume of Ga in terms of absorption coefficient vs. wavelength for CdSe:Ga. It can therefore be found that $\alpha$ has increased in general for all samples, with an increase of Ga (Fig 7).
c) Optical energy gap: In order to calculate the band gap energies of thin films for CdSe and CdSe:Ga, the plot of \((\alpha h \nu)^2\) as an incident radiation energy feature (Fig 8). The energy band gap is obtained from intercept of the extrapolated linear part of the curve with the energy axis at \((\alpha h \nu)^n = 0\), it is observed that direct band gap of the CdSe and CdSe:Ga films. The effect of doping concentration on the direct band gap values for CdSe thin film. The results show that increased Ga levels lead to a lower band difference (Fig 9). The band gap values are attributed to the thin film's crystallinity. This reduction in energy spacing may be due to the forbidden impurities, resulting in donor levels forming within the energy spacing near the conduction band. The \(E_g\) values for direct band gap for all the thin films are summarized in Table (5). Thus, it will absorb lower-energy photons that fit other workers' findings [23].

Fig 8: \((\alpha h \nu)^2\) versus photon energy gap of CdSe and CdSe:Ga with different dopant.
Table 5: summary obtained by the results of optical energy gap of CdSe and CdSe:Ga at different doping.

| Dopant percentage. | energy gap (eV) |
|-------------------|-----------------|
| pure              | 1.75            |
| 1%                | 1.70            |
| 3%                | 1.68            |
| 5%                | 1.62            |

Fig. 9: shows the change of the energy gap with the doping ratio.

4. Conclusions

CdSe and CdSe:Ga were successfully prepared from pure elements Cd, Se and Ga. XRD patterns showed the CdSe and CdSe:Ga films are polycrystalline of hexagonal structure directions by Ga doping that orientated a peak became less intensity from undoped CdSe film. The XRD patterns and AFM measurements of Ga-doped and undoped CdSe thin films agree with each other of the grain size within nanocrystal range and decrease as Ga doping concentration increases. AFM images indicate that the increasing in Ga doping that showed smooth surface films compared to the CdSe films. The optical bands gaps of the films have a direct band transition and slightly decreased with the increasing Ga doping.

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