Study of the Optical properties for CdS before and after irradiated by CO₂ laser for different exposure times

Najat A. Dahham
Department of Physics, College of Science, Tikrit University, Tikrit, Iraq
najat_200570@yahoo.com

Abstract
Cadmium sulphide (CdS) thin films were deposited on glass substrates using thermal vacuum evaporation technique at pressure ($10^{-6}$) Torr at room temperature then samples irradiated by CO₂ laser of power (1 watt) and wave length (10.6) μm at distance 10 cm from the source during different exposure times (3, 5, 10, 15) sec. The absorbance spectra was recorded using UV-visible spectrophotometer. Optical properties such as transmission, reflection, absorption coefficient ($\alpha$), optical band gap ($E_g$), extinction coefficient (K), refractive index (n), and complex dielectric constants ($\varepsilon_i$&$\varepsilon_r$) were evaluated from absorbance spectra. The results shows that the laser irradiation cause increase in reflectance R, absorption coefficient $\alpha$, the extinction coefficient K, the refractive index n and the real part and imaginary part of dielectric constant while irradiation cause decrease in the transmittance T and the value of the energy gap $E_g$.

Keywords: Cadmium Sulfide (CdS), thin film, Thermal evaporation, laser irradiation, optical properties.

Introduction
Over the years, Metal chalcogenides (Sulfides, tellurides and selenides) have received more attention for researchers because of optoelectronic applications such as photodetectors, solar cells, thin film transistors etc. Cadmium sulfide (CdS) is an important metal chalcogenides CdS thin films are regarded as one of the most promising materials for heterojunction thin film solar cells. CdS is one of the important II –VI group semiconductor with a direct band gap of 2.42 eV [1,2], and used as the window material together with several semiconductors such as CdTe, Cu₂S, InP and CuInSe₂ with 14 – 16% efficiency [3, 4]. Many techniques have been reported for the deposition of CdS thin films. These include evaporation, sputtering, chemical bath deposition, spray pyrolysis, metal organic chemical vapour deposition (MOCVD), molecular beam epitaxy (MBE) technique, electrodeposition, photochemical deposition etc. [5-9]. In the present work, thermal evaporation technique has been chosen for the deposition of CdS thin films as it is simple compared with other new and sophisticated techniques. Here, we report a detailed study on the optical properties of such CdS thin films as the knowledge of the optical properties of these films is very important in many scientific, technological and industrial applications in the field of optoelectronic devices, particularly solar cells. Laser crystallization of thin films on glass is widely used to improve the electronic transport. In the production of flat panel displays, laser crystallization increases the carrier mobility in thin film transistors. Suitable laser intensity profiles in combination with multiple scanning sequences have been used to reduce the number of grain boundaries[10]. Laser crystallization appears to be more promising compared to the thermal crystallization as it does not damage the glass substrate and that almost all of the laser energy is directly absorbed into the CdS film [11]. Among molecular lasers, the CO₂ laser is of greatest practical importance. The high level of efficiency with laser in which laser radiation can be generated in continuous wave (CW) and pulse operation is its most fascinating feature. In atom and ion lasers, laser radiation is the result of the electron transitions close to the limit for single or double ionization. The infrared radiation of the CO₂ laser on the other hands is the result of the energy exchange between rotational- vibrational levels within the electron ground level [12].

Experimental part
CdS thin film was prepared by using thermal vacuum evaporation technique type Edward under the pressure ($10^{-6}$) Torr on glass substrate at room temperature. Thickness of the films has been carried out by weighting method and the measured thicknesses were about (1000 Å). The thin films were irradiated by using CO₂ laser of power (1 watt) and wavelength (10.6 μm) at distance (10 cm) from the source during different exposure times (3, 5, 10, 15) sec. After the formation of the films and irradiated, the absorbance spectra was recorded using UV-Visible spectrophotometer type centra-5 in the range of wave length (180-1100) nm at room temperature.

Theoretical part
The measured absorbance (A) of the sample can be used to calculate the transmittance (T), using the relation:

$$ T = \log 1/A \quad (1) $$

Whereas the reflectance (R) was calculated from the following relation [13]:

$$ R = 1 - A - T \quad (2) $$

The absorption coefficient $\alpha$ was calculated using Lambert law [14]:

$$ \ln \left( \frac{I_0}{I} \right) = 2.303 \, \lambda = \alpha \, t \quad (3) $$

where $I_0$ and $I$ are the intensity of incident and transmitted light respectively, and $t$ the film thickness.

$$ \alpha = 2.303 \, \lambda / t \quad (4) $$

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The relation between the absorption coefficient and photon energy \( h\nu \) is given by [15]:

\[
\alpha h\nu = (h\nu - E_g)^n \quad \text{(5)}
\]

Where \( E_g \) is the energy gap and \( n = \frac{1}{2} \) for allowed direct transition and \( n = 2 \) for allowed indirect transition.

The extinction coefficient was calculated from the relation [16]:

\[
K_o = \frac{\alpha \lambda}{4\pi} \quad \text{(6)}
\]

Where \( \lambda \) is the wavelength.

The refractive index (n) is the relative between speeds of light in vacuum to its speed in material which does not absorb this light. The value of n was calculated from the following formula [9]:

\[
R = \frac{K_r - 1}{K_r + 1} \quad \text{(7)}
\]

The real \( (\varepsilon_r) \) and imaginary \( (\varepsilon_i) \) parts of dielectric constants are obtained by using the relations [16]:

\[
\varepsilon_r = n^2 - K_o \quad \text{(8)}
\]

\[
\varepsilon_i = 2nK_o
\]

**Results and discussion**

The absorption value of un-irradiated sample increase with increasing photon Energy because when photon energy incident equal or greater than the value of band gap energy cause direct transition from valance band to conduction band [17]. Also figure (1) show increasing in the value of the absorption after irradiation by CO2 laser and increasing with increasing period of irradiation, because the irradiation causes some structural defects in the films [18], these may be attributed to the creation of energy states in the region between the conduction and valance band that will be available for the incident photon to be absorbed.

**Fig (1) The absorbance versus photon energy for sample before and after irradiation**

The plot of transmission data versus photon energy is shown in fig (2) which shows that the transmission reach a maximum value in the lower photon energy and decrease with increasing photon energy for samples under investigation. It can be noted that the transmission decrease with increase the period of sample irradiation by CO2 laser, because the absorption value increases.

**Fig (2) The Transmission versus photon energy for sample before and after irradiation**

**Fig (3) The Reflectance versus photon energy for sample before and after irradiation**

Variation of optical absorption coefficient with photon energy for Cds films before and after irradiation with CO2 laser during different times irradiation are shown in Figure (4). It shows that the absorption coefficient increases slowly at the higher wavelength region and then increases sharply near the absorption edge. This increasing in the absorption coefficient due to from increasing in the absorption according to equation (4). The absorption coefficient is found increasing after laser irradiation of the thin film. This is possibly due to the increase in grain size and the decrease in the number of defects [8].
Fig (4) The absorption coefficient versus photon energy for sample before and after irradiation

The plots of $(\alpha h\nu)^2$ versus $h\nu$ are shown in figures (5-9) for CdS thin films before and after irradiation with CO$_2$ laser respectively. Variation of $(\alpha h\nu)^2$ with $h\nu$ for CdS films is a straight line, indicating the presence of a direct transition. Band gap energy $E_g$ was determined by extrapolating the straight-line portion to the energy axis for zero adsorption coefficients $\alpha$. The decrease in band gap shows that the irradiated film causes a strong ‘red shift’ in the optical spectra due to sintering of the nanocrystalline into larger crystallites. Lozaca-Morales et al. [19] have reported that while the lattice parameter and grain size are increased, the optical band gap is decreased. These changes have been attributed to the crystallite size-dependent properties of the energy band gap. The presence of a high concentration of localized states would produce absorption at energy less than the band gap and thereby is responsible for such low values. The weak absorption region at lower energy side is attributed to the presence of intraband transitions at localized states in the gap. It is clearly observed from figures that the optical gap is lowered from 2.46 eV before irradiation to 2.34 eV after laser irradiation during 15 sec the well-known effect of photodarening [20,21] and these results are good agreement with the results in the researches [8, 22-25]. The energy gap for for sample before and after irradiation showed in table (1)

As seen also as a result of irradiation, the absorption edge shift to longer wavelengths which confirm the photodarkening. The red shift manifests the fact that Urbach tail light can generate mobile carriers, holes in present CdS thin film.

<table>
<thead>
<tr>
<th>Energy gap before irradiation (eV)</th>
<th>Energy gap after irradiation at 3 sec (eV)</th>
<th>Energy gap after irradiation at 5 sec (eV)</th>
<th>Energy gap after irradiation at 10 sec (eV)</th>
<th>Energy gap after irradiation at 15 sec (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.46</td>
<td>2.42</td>
<td>2.41</td>
<td>2.40</td>
<td>2.34</td>
</tr>
</tbody>
</table>

Table (1): The energy gap for for sample before and after irradiation

Fig (5) The $(\alpha h\nu)^2$ versus photon energy for sample before irradiation

Fig (6) The $(\alpha h\nu)^2$ versus photon energy for sample after irradiation at 3 sec
extinction coefficient depends on absorption coefficient $\alpha$ according to equation (6).

The variations in the refractive index as a function of photon energy is shown in figure (11). It can be noticed that the refractive index increased with increasing photon energy and it increased with increasing the time of irradiation this behavior is similar to the reflectance behavior.

The variations in real part and imaginary part of dielectric constant, as a function of photon energy are shown in figure (12). It can be noticed that the real part and imaginary part of dielectric constant increased after irradiation. The high value of the real part of dielectric constant indicate that the CdS films have ability to polarize. and it is observed that the plot shape of $\varepsilon_r$ as the same shape of $n$, that is because $\varepsilon_r$ values depend on $n$, $K$ values.
Fig (12) (a) the real part dielectric constant (b) imaginary part dielectric constant versus photon energy for sample before and after irradiation

Conclusions
CdS thin films were prepared using thermal evaporation technique on glass substrate under vacuum equal to \(10^b\) torr. The effects of different exposure times of CO\(_2\) laser on PbS thin films are:

References
دراسة الخواص البصرية لغشاء CdS قبل وبعد التشعيع بليزر CO$_2$ وبأزمان تشعيع مختلفة

نجاة أحمد دحام
قسم الفيزياء، كلية العلوم، جامعة تكريت، تكريت، العراق

najat_200570@yahoo.com

الملخص

تتم في هذه الدراسة تحضير أغشية رقيقة من مادة CdS المحضرة بطريقة التبخير الحراري الفراغي تحت ضغط ($10^{-6}$ torr) على قواعد من الزجاج في درجة حرارة الغرفة وتم تشعيع العينات بليزر CO$_2$ ذو طاقة (1 watt) وعلى بعد (10.6μm) وعلى بعد (10 Cm) من المصدر وتم تسجيل طيف الإمتصاص باستخدام مطياف UV-visible ومنه تم حساب بعض الخواص البصرية والتي تتضمن النفاذية، الانعكاسية، فجوة الطاقة، معامل الإمتصاص، معامل الخضوع معامل الإكسار وثابت العزل الحقيقي والخيالي. ومن نتائج الدراسة أن التشعيع بالليزر أدى زيادة في الانعكاسية، معامل الإكسار، معامل الخضوع K، معامل الأكسار α، ثابت العزل n، ثابت العزل R، ثابت الإكسار K، ثابت الإكسار R، ثابت طاقة الفجوة الفعلية والخيالي بينما التشعيع أدى إلى نقصان في النفاذية T وفي قيمة فجوة الطاقة $E_g$.  

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