# Preparation of Nanocrystalline Copper Doped CdS Thin Films by Spray Pyrolysis Method

**Najiba Abdullah Al-Hamdani** **Ameer Abdul Hussain Salih**
Physics Department, Education College – Al-Mustansiriya University

## ASTRACT

Nanocrystalline undoped and Cu-doped thin films have been prepared on glass substrates at 673 K by spray pyrolysis CSP. The effect of Cu-doped on structural and optical properties was studied. XRD data indicates the formation of hexagonal nanocrystalline CdS and CdS:Cu thin films, and $Cu^{2+}$ ions entering the lattice substitutionally. The optical properties of these films were studied by measuring their optical transmission and their absorption spectra in the 300-900 nm range. The optical absorption studies reveal that the transition is direct with band gap value (2.417eV) for undoped and in the range (2.413-2.4eV) for doped films. Other important optical constants, such as extinction coefficient, refractive index and dielectric constant was calculated and analyzed.

**Key words:** Nanocrystalline thin films , spray pyrolysis

# Preparation of Nanocrystalline Copper Doped CdS Thin Films by Spray Pyrolysis Method

Najiba Abdullah Al-Hamdani Ameer Abdul Hussain Salih

# تحضير أغشية CdS الرقيقة النانويه غير المشوبة والمشوبة بالنحاس بطريقة الترسيب الكيميائي الحراري

نجيبة عبدالله الحمداني أمير عبد الحسين صالح

قسم الفيزياء – كلية التربية – الجامعة المستنصرية

## الخلاصة

تم تحضير أغشية CdS الرقيقة النانويه غيرالمشوية والمشوبة بـ Cu بطريقة الترسيب الكيميائي الحراري على قواعد زجاجية وبدرجة حرارة (673 k). تم دراسه تأثير الشائبه Cu على الخصائص التركيبية والبصريه .اظهر طيف الاشعة السينية بان جميع الاغشية هي سداسيه ونانويه وان الشائبه تحتل مواقع بينية داخل الشبيكه .درست الخصائص البصريه من طيف النفاذيه والامتصاصيه على مدى من (300-900 nm). وبينت الامتصاصية البصريه على ان الانتقالات الالكترونيه هي انتقالات مباشره وبفجوة طاقه بصريه (2.417 eV) للغشاء غير المشوب وبحدود (2.417-2.4eV) للاغشيه المشوبه . تم حساب الثوابت البصريه الاخرى والمتمثله بمعامل الخمود، معامل الانكسار وثابت العزل ثم تحليل النتائج.

## INTRODUCTION

Cadmium sulfide CdS thin film is one of the II-VI compound semiconductors and is composed of hexagonal wurtzite crystal structure. CdS has a wide band gap (2.42eV) and is a direct transition semiconductor [1]. Consequently, it is potentially an important material to used as an antireflection coating for heterojnction solar cells [2], or as a window material in high efficiency with film solar cells based on CdTe or CIGS [1]. Because of such an extended area of application for these materials, CdS thin films were deposited by various techniques, such as physical vapor deposition [3], chemical bath deposition [4-5], sputtering [6], spray pyrolysis CSP [7-9] and etc. Spray pyrolysis is one of the most used methods and has continuous operation, very low cost and simple technique that enables intentional doping and getting large area and uniform thin films [7]. Pure and doped CdS has been extensively studied [1,7-11]. It is found that, the physical properties depend on the preparation technique and addition of different elements on pure CdS such as Fe, Al, Ga, Cu, In, .etc.

In this work CdS and CdS:Cu thin films prepared by spray pyrolysis and to investigate the effects of doping ratio CdS:Cu on the structural and optical properties.

## EXPERIMANTAL DETAILS

The pure CdS and CdS:Cu thin films were deposited by spraying an aqueous solution of $CdCl_2$ (0.1M) and thiourea (0.1M) with ratio 1:1 . To find out the effect of Cu, (0.1M) of an aqueous solution of ($CuCl_2$). $CuCl_2$ is added to the mother solution with different volumes (0-10) %. The films were deposited onto glass substrates at a 673K substrate temperature. The temperature of substrate was controlled by an Iron-constantan thermocouple. The thickness of all the thin films was (390±5 nm) measured by weight difference method using sensitive balance (Metter Hk160).

The X-ray diffraction patterns of the films were recorded with (PHILIPS PW1840) Xray diffractometer operating with a 1.5406 nm monochromatized Cu-$k_\alpha$ radiation at 40 KV and 30 mA in the range (20-60 deg) with speed 5 deg/min.

Transmission T and absorption A of the prepared films were measured with a double beam spectrophotometer within the wavelength range of 300-900nm.

## RESULTS AND DISCUSSION

Fig. (1) shows the X-ray diffraction patterns of CdS and CdS:Cu films with different copper concentrations. All the peaks in the patterns correspond to hexagonal structure of CdS. No change in the characteristic peak positions was observed in samples doped with Cu. This means that the doped CdS samples retain the hexagonal structure. It was observed that there is a change in the height and broadening of the peaks could be attributed to the change in the scattering factor corresponding to incorporated element. No phase corresponding to Cu/CuS/CuO/CdO or other copper compounds was detected in the XRD, which indicates that incorporation of $Cu^{2+}$ ions does not change the crystal structure of the CdS film.

It can be seen an increase of peak intensity of (002) plane with respect of (101) plane with increase of dopant concentration this behavior was observed by others [10, 12]، this mean that C-axis of CdS films change from inclined to the substrate to perpendicular to substrate. The average (101) interplaner distance $d_{(101)}$ was calculated using the formula [1].

$$n\lambda = 2d\sin\theta \qquad (1)$$

As shown in fig.(2) the spacing of the ($d_{(101)}$) lattice plane decrease with increase Cu/Cd ratio. Now, since the ionic radius of $Cu^{2+}$ (0.96 Á) is smaller than that of $Cd^{2+}$ (1.03 Á) [13], this suggests that $Cu^{2+}$ ions replace the $Cd^{2+}$ ions in the lattice substitutionally, which in turn results in a smaller d value than that of undoped CdS film. There is always the possibility that some of the $Cu^{2+}$ ions enter the lattice interstitially but since the d value continues to decrease as the Cu concentration increase ratio increases, it is more likely that the majority of $Cu^{2+}$ ions are replacing $Cd^{2+}$ ions substitutionally , this is observed by other workers [1,9-11].

The grain size was calculated using the formula: [14]

$$D = \frac{0.9\lambda}{\beta \cos\theta} \qquad (2)$$

Where β is full width at half maximum (FWHM) in radians. It can be seen from table (1) all the values of grain size are in the nano scale.

The morphological features of CdS thin films were examine using AFM microscope. AFM micrographs were recorded from different regions of the samples, using sampling areas of 5 μm x 5 μm.

In Fig. (3) we present some AFM images for the investigated CdS samples.

AFM images showed that all samples present well defined nanosized grains, having a roughness (RMS) values, ranging from 15 nm to 61 nm, as can be seen from the table (1) Fig.(4) shows plots of transmission spectra versus wave length for the films studied. Spectra of all films shows that the optical transmission decreases with increases of Cu content, this may

be due to increase scattering of photons by crystal defects and the free carrier absorption of photons is contributed to the reduction in optical transmittance [6]. Also it can be seen that the transmittance decreases at low wavelength region ($\lambda$<500 nm) which is the spectral region of edge absorption, in this region the incoming photons have sufficient energy to excite electrons from the valence band to conduction band and thus these photons are absorbed within the material to decrease the transmittance. For this reason, this region carries the information of the band gap of the material [7].

The optical absorption coefficient $\alpha$ was determined by using the following equation [13].

$$\alpha = \frac{1}{t} \ln T \qquad (3)$$

Where T is transmittance, t is film thickness. The optical absorption edge was analyzed by the following equation: [15]

$$\alpha h\upsilon = B(h\upsilon + E_g)^{\frac{1}{2}} \qquad (4)$$

Where B is a constant .It has been observed that the plots of $(\alpha h\upsilon)^2$ versus $h\upsilon$ are linear over a wide rang of photon energies indicating the direct type of transition as in fig(5) . The intercepts of these plots on the energy axis give the energy band gaps Eg and were listed in table (1) As shown, the band gap of undoped film has a band gap of (2.417eV) which agrees with the (2.42eV) band gap of single crystal CdS [13], and the band gap of doped films decreases with increases of Cu concentration. It has been suggested by Lokhande and Pawar [14] that in case of Cu-doped CdS films, incorporation of $Cu^{2+}$ ions as well as sulfur deficiency in Cu-doped films gives donor levels in the band gap of CdS. As the $Cu^{2+}$ concentration increases, which in turn increases the donor levels, it become degenerate and merge in the conduction band gap of CdS, causing the conduction band to extend into the band gap, which reduces the band gap. These results are quite similar to those obtained by other workers [15].

The optical constants such as extinction coefficient k, refractive index $n_0$ and dielectric constant (real and imaginary part) were calculated from the following equation [8]

$$k = \frac{\alpha\lambda}{4\pi} \quad (5)$$

$$n = \left[\left(\frac{1+R}{1-r)}\right)^2 - \left(k^2+1\right)\right]^{\frac{1}{2}} + \frac{1+R}{1-R} \quad (6)$$

$$\varepsilon_r = n^2 - k^2 \quad (7)$$

$$\varepsilon_i = 2nk \quad (8)$$

Where R is the reflectance, and $\varepsilon_r$, $\varepsilon_i$ are real and imaginary part of dielectric constant respectively. It can be observed from fig.(6) and fig.(7) the variation of extinction coefficient and refractive index with photon energy, and both extinction coefficient and refractive index increase with increasing $Cu^{2+}$ concentration this is due to increase of absorption coefficient.

Variation of real part and imaginary part of dielectric constant are shown in fig. (8) and fig. (9) respectively. It is seen that both parts follow the same pattern and it is seen that the values of real part are higher than those of the imaginary parts. The real part generally relates to dispersion, while the imaginary part provides a measure to dissipative rate of the wave in the medium [11].

## CONCLUSION

Copper in situ doping of CdS using CSP method was proved successfully. The XRD analysis showed that deposited films were polycrystalline nature with hexagonal structure and did not detect any new peaks due to Cu-doping indicating that incorporation of $Cu^{2+}$ ions does

not change the crystal structure of the CdS films. The transmission and optical energy gap decrease with increase Cu concentration. Extinction coefficient, refractive index and real and imaginary of dielectric constant increase with increase Cu concentration

## References

1. H. Khallaf, I. Oladeji, L. Chow,Thin Solid Films,516(2008)5967.
2. E. Cuculescu, I. Evtodiev, M. Caraman, M. Rusu, J. of Optoelectronic and Advanced Materials, Vol.8, No.3 (2006) 1077.
3. R. Birkmire, B. Mccandless, S.Hegedus, Int. J. Sol. Energy, 12(1992)145.
4. P. Roy, S. Srivastava, Matt, Chem. Phy. 95(2006)235.
5. S. Linsi, B. Kavitha, M. Dhanam, and B. Maheswari, J. World Appl. Sciences, Vol.10, No.2 (2010) 207.
6. C. Tsai, D. Chuu, G,Chen, S. Yang, J. Appl. Phys., 79 (1996) 9105.
7. J. S. Ikkhmayies, N. R. Ahmad-Bitar, Jordan J.Mechan. and Indus. Engin. Vol.4 No.1 (2010)111.
8. S. Ilican, M. caglar, Y. Caglar, J. Optoelectronic and advanced materials, Vol.9 No.5 (2007) 1414.
9. L. I. Soliman, H. H. Afify and I. K. Battisha, indian J. Pure and Appl. Phys., Vol.42(2004)12.
10. H. Khallaf, G. Chai, O. Lupan, L. Chow, S.Park, A. Scuite, Appl. Surf. Scien. 255(2009)4129.
11. H. Khallaf, G. Chai, O. Lupan, L. Chow, S.park, A. Scuite, J. Phys. D. Appl. Phys. 41(2008)1.
12. H. H. Afify, I. K. EL ZawaiI, I. K. Battisha, J. Materials Sciences Materials in Electronics 10 (1999) 497
13. J. Huheey, Inorganic Chemistry, 3rd ed. Harper and Row, New York (1983).
14. C. Gumus, O.M. Ozkender, H. Kavak, Y. Ufaktepe, J. Optoelectronic and Advanced Materials, Vol.8, No.1 (2006) 299.
15. A. Ashour, Turk. J. Phys., 27 (2003) 551.

**Table (1) Show the value of grain size for pure CdS and incorporation with different Cu content and energy gap Eg for pure CdS**

| CdS:Cu (%) | Grain size (nm) | Eg (eV) | Roughness average nm | RMS nm |
|---|---|---|---|---|
| CdS | 45.2 | 2.417 | 9.81 | 12.7 |
| CdS :Cu (2%) | 43.0 | 2.413 | 29.00 | 37.5 |
| CdS :Cu (4%) | 40.0 | 2.410 | 28.90 | 37.1 |
| CdS :Cu (6%) | 42.1 | 2.408 | 45.80 | 61.8 |
| CdS :Cu (8%) | 46.6 | 2.405 | 41.00 | 53.2 |
| CdS :Cu (10%) | 40.7 | 2.400 | 41.50 | 51.3 |

# Preparation of Nanocrystalline Copper Doped CdS Thin Films by Spray Pyrolysis Method

Najiba Abdullah Al-Hamdani Ameer Abdul Hussain Salih

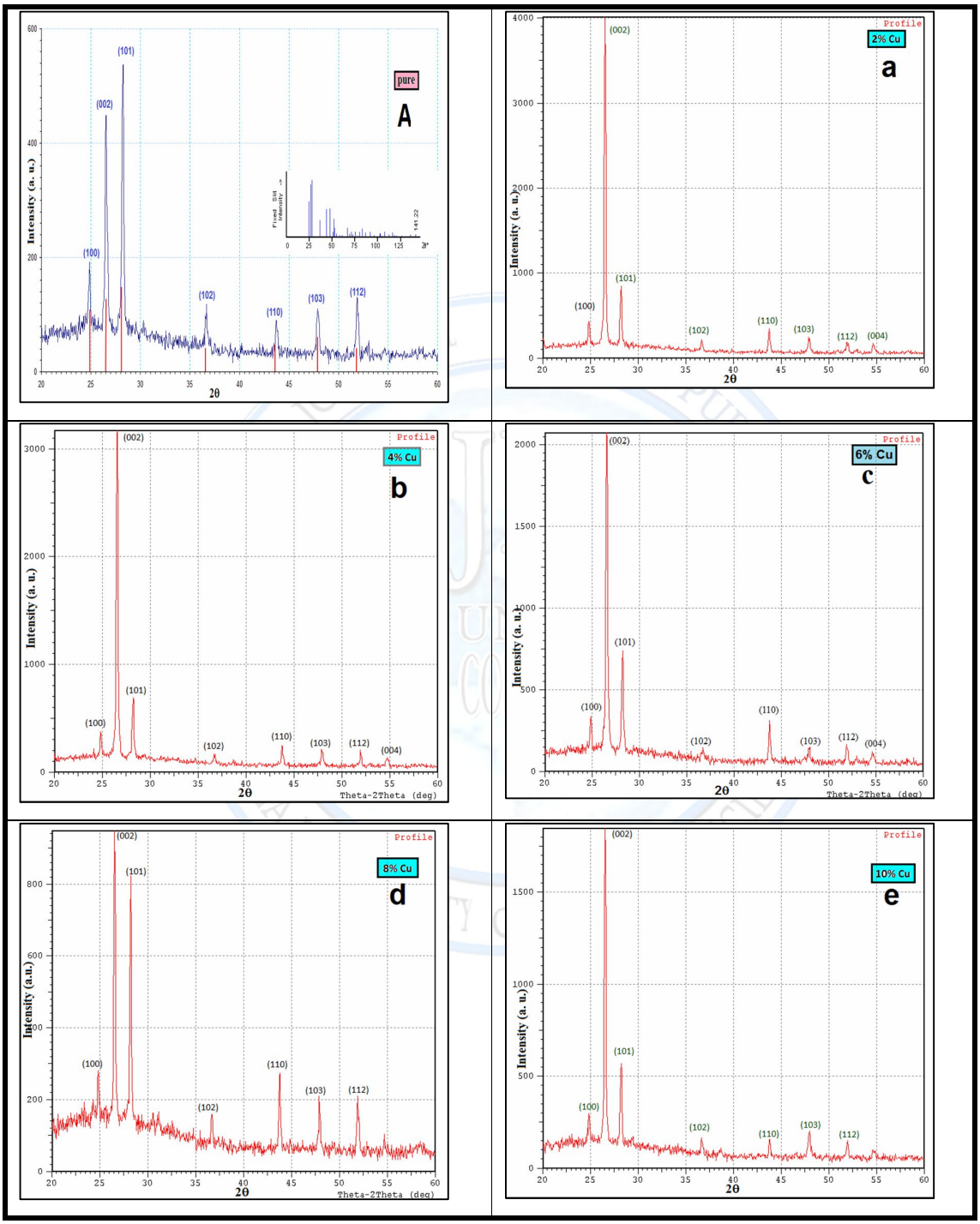



**Fig. (1) X-ray diffraction patterns of CdS and CdS:Cu thin films with different concentration**

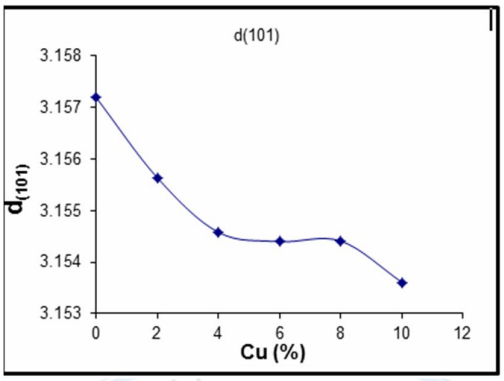
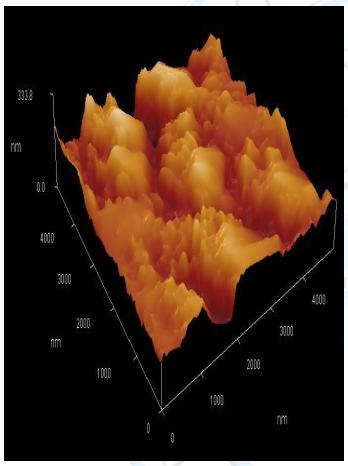
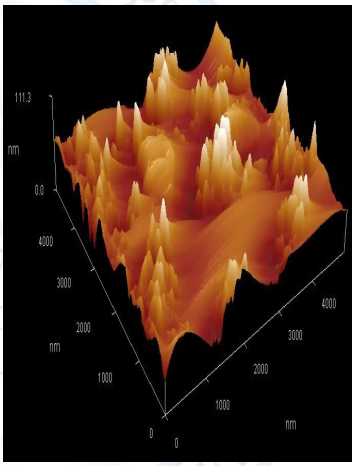


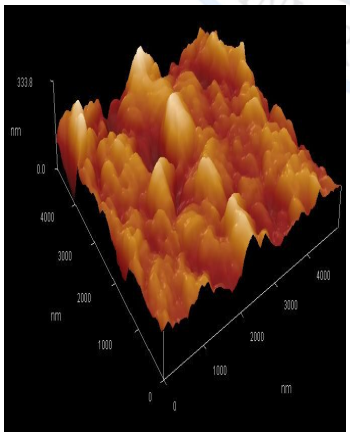

**Fig.(2) $d_{(101)}$ as a function of Cu content**



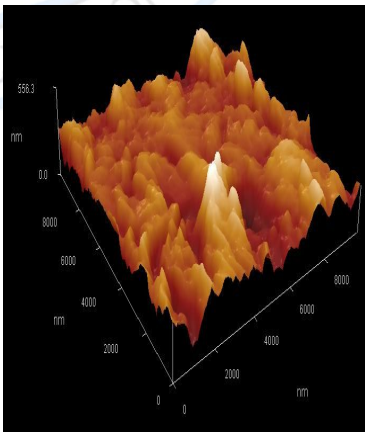
Pure



2%



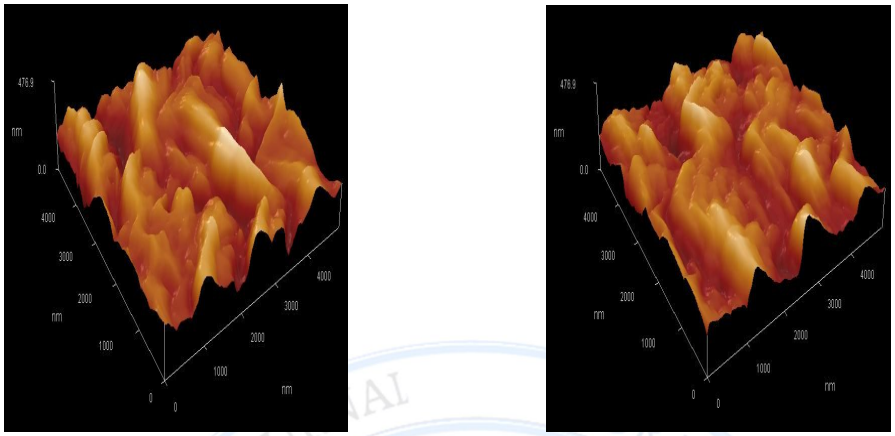
4%



6%

**Preparation of Nanocrystalline Copper Doped CdS Thin Films by Spray Pyrolysis Method**

**Najiba Abdullah Al-Hamdani** **Ameer Abdul Hussain Salih**



8% 10%

**Fig(3) Three-dimensional atomic force microscopy images of films deposited at various Cu concentration**

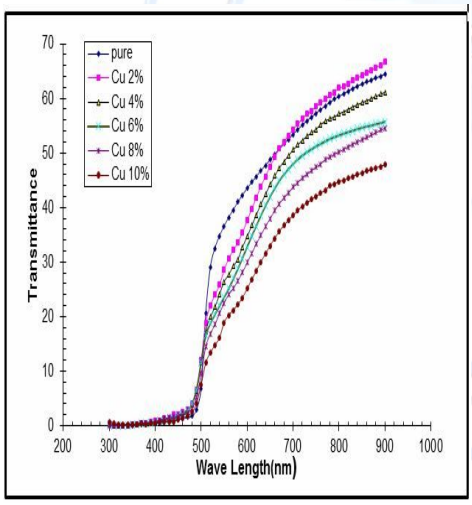



**Fig.(4) Transmittance of pure CdS and CdS:Cu films**

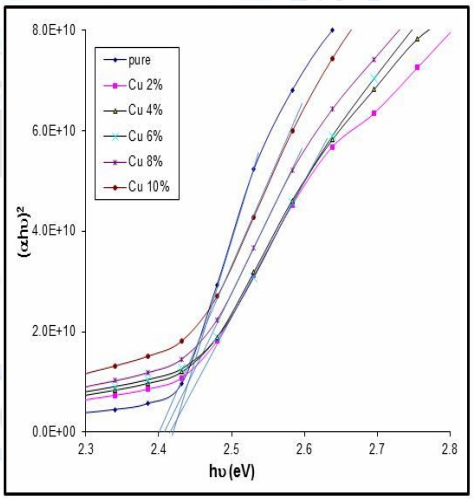



**Fig.(5) Relation between $(\alpha h\upsilon)^2$ and $h\upsilon$ for pure CdS and CdS:Cu films**

**Preparation of Nanocrystalline Copper Doped CdS Thin Films by Spray Pyrolysis Method**

**Najiba Abdullah Al-Hamdani** **Ameer Abdul Hussain Salih**

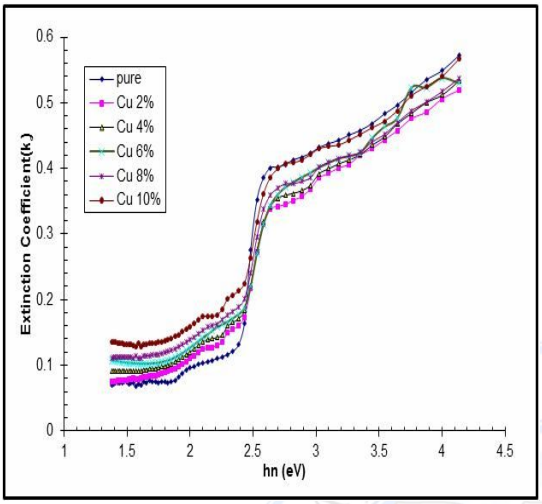



**Fig.(6) Extinction coefficient of pure CdS and CdS:Cu films**

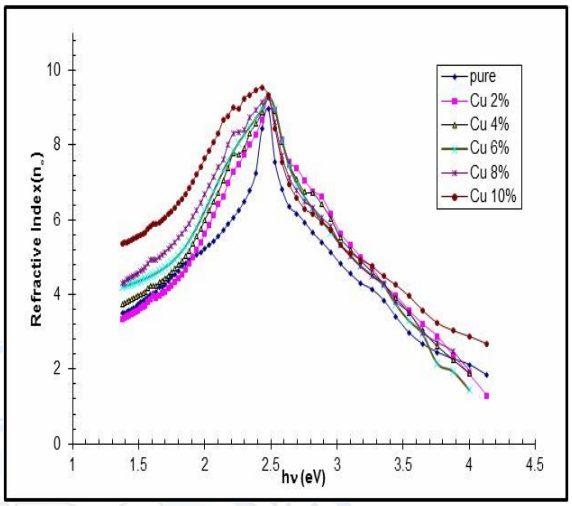



**Fig.(7) Refractive index of pure CdS and CdS:Cu films**

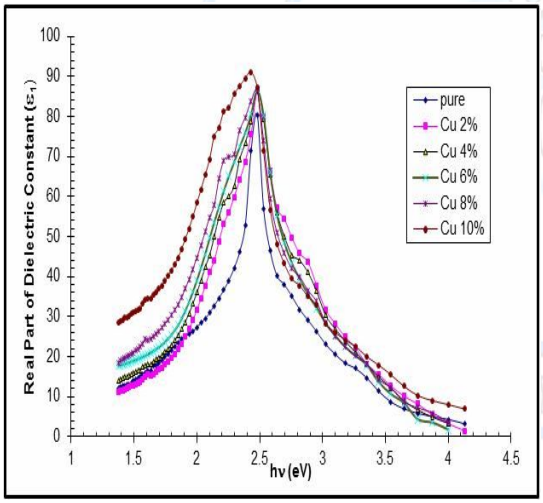



**Fig.(8) Real part of dielectric constant of pure CdS and CdS:Cu films**

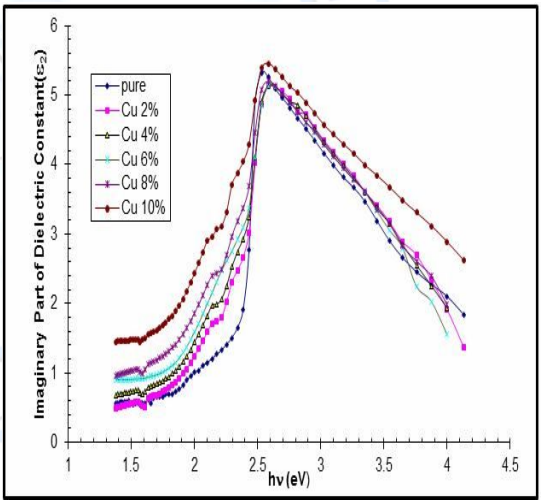



**Fig. (9) Imaginary part of dielectric constant of pure CdS and CdS:Cu films**