

## Effect of Annealing Temperature on the Optical Properties of Nano-Structure CdS Embedded in Silica Gel Thin Film Prepared by Sol Gel Technique.

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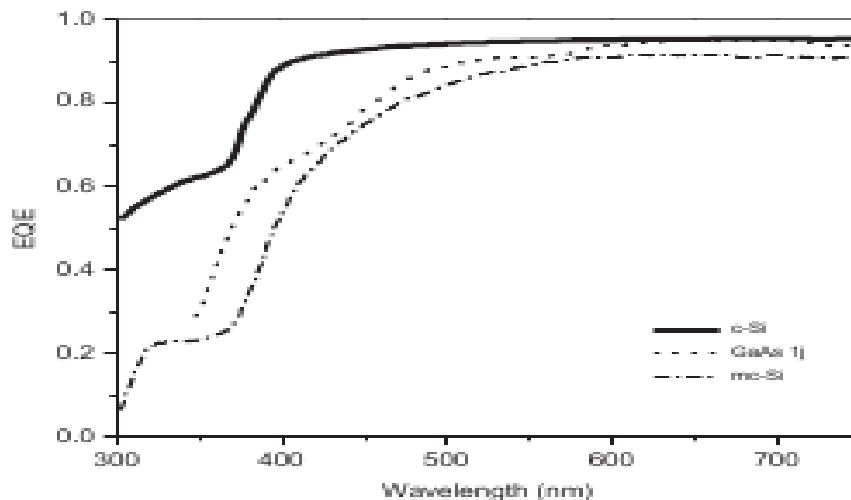
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**Abstract:** The effect of increasing the annealing temperature on the CdS incorporated in silica xerogel thin film glasses is evaluated. The thin film samples are prepared via silica gels containing solution mixture of (CdCl<sub>2</sub> and thiourea) with molar ratio 1:1, 5 mol % from this mixture solution was added to the host silica gel precursor. X-ray diffraction and Scanning electron microscope make it possible to evaluate the sample structure and the morphology. The absorption edge exhibited a blue shift by decreasing the annealing temperature, and its energy shift was reciprocally proportional to the radius. The energy band gap shifted upward in energy for smaller nano-particle size.

**Key words:** Nano-structure, CdS: silica xerogel, CdCl<sub>2</sub>: thiourea mixture solution, XRD, optical, band gap energy.

### INTRODUCTION

The behavior of the solar cell towards a photon wavelength can be described using a term called External Quantum Efficiency (EQE) which defined as the number of collected carriers per each photon with wavelength  $\lambda$ . Figure 1 show (EQE) for some solar cell material as a function of wavelength. We can see the same trend in all curves where the EQE is low at UV region and it increases by moving towards the visible light region so absorption and collection process will be optimized at visible light region and it is poor at ultraviolet region.



**Fig. 1.3:** External Quantum Efficiency (EQE) verses wavelength ( $\lambda$  in nano meter).

If we could convert the photons at which the solar cell have low External Quantum Efficiency (EQE) (UV photons) to photons at which the solar cell have high External Quantum Efficiency (visible light photons) so the number of collected carriers per photons will increase and the solar cell efficiency will be enhanced.

Nano particles have attracted great interest in recent years because of their unique physical and chemical properties, which are different from those of either the bulk material or single atoms (Alivisatos 1996; Kamal *et al.* 2011, Battisha *et al.* 2009, Badr *et al.* 2011; Battisha 2002), so intensive researches made on nano materials which produces massive application and now nano- technology applications can be seen in all field of life. Electronic and optical properties of semiconductor show a great dependence on the particle size which, can be illustrated by the dependence of the semiconductor band gap into the particle size and according to effective mass approximation (Brus 1984; Dutta *et al.* 2009) the band gap increases by decreasing the particle size so by controlling the particle size one can have a tunable optical and electric properties. Cadmium Sulphide is one of

luminescent II-VI semiconductor family which is promising material for applications in biology, solar cell and gas sensor (Chahboun *et al.* 2006). The CdS nano particles have a large percentage of surface atom so it is very active under ambient condition, in order to protect these nano particles it were embedded in a host material such as silica matrix (SiO<sub>2</sub>). SiO<sub>2</sub> matrix has good optical and mechanical properties and have very large band gap so the absorption and emission of SiO<sub>2</sub> don't affect the absorption and emission of nano CdS particle. Sol gel method have been well tested and adopted to fabricate nanoparticles in a controlled fashion (Parvathy *et al.* 1997). Sol gel method have also many advantage like low temperature technique, low cost materials and equipment and the possibility to get the final product in different form (thin film, bulk, and powder) (Badr *et al.* 2008; Battisha *et al.* 2007; Battisha 2007; Battisha *et al.* 2007; Badr *et al.* 2011).

The aim of the present work is to prepare nano-structure silica gel incorporated with constant concentration of CdS at 5 mol % using sol gel technique. Optical properties were studied in the range between 200 and 1000 nm. The structural properties will be evaluated by XRD.

### Experimental:

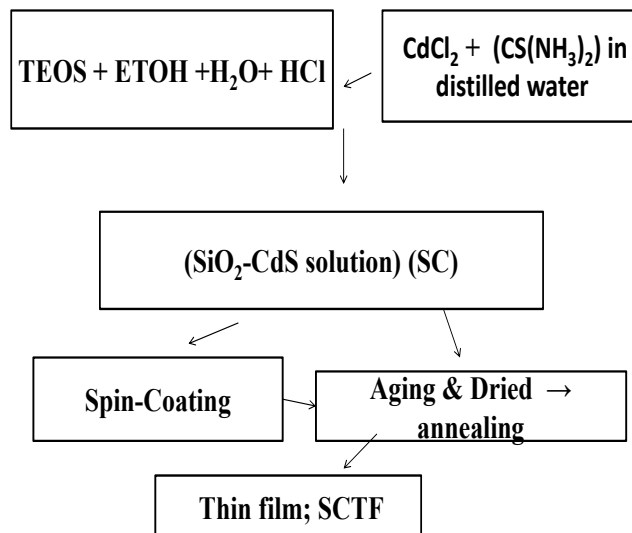
Silica gel incorporated with nano-particle CdS (SC) is successfully prepared using sol gel technique in thin film form (SGTF) as shown in the flow chart, Fig. 1.

Synthesis of silica gel incorporated with 5 mol % of CdS, SiO<sub>2</sub> (100-x, x= 5 mol %) CdS thin film, S5CTF is prepared at three different annealing temperature 250, 300 and 400°C, respectively. Pure silica gel was prepared using the acid catalyst procedure via the hydrolysis and poly-condensation of (C<sub>2</sub>H<sub>5</sub>OH)<sub>4</sub>Si, tetra-ethyl-ortho-silicate (Teos), ethanol and distilled water, in the presence of hydro chloric acid, with Molar ratios, Teos: C<sub>2</sub>H<sub>5</sub>OH: H<sub>2</sub>O: HCL = 1:7:5:0.035 respectively.

The obtained homogeneous solutions of CdCl<sub>2</sub> and thiourea were aged for about two days at room temperature before dispersed with a spun of 3500 rev. /min for 30 seconds on a glass substrate. At least two successive coatings were required to provide suitable effective film thickness. After finishing the coating process, the films dried for 30 min and then sintered at different temperature 200, 250, 300 and 400°C, in a muffle furnace with heating rate 2.5°C/min (Battisha 2002).

X-ray diffraction (XRD) patterns of the prepared samples were recorded with X-ray diffractometer using mono-chromatized CuK<sub>α1</sub> radiation of wavelength = 1.54056 Å. Crystallite sizes G were determined using Scherer's equation ( $G = K\lambda / D \cos\theta$ ), where K is the Scherer constant (0.9),  $\lambda$ : is the wavelength, and D is the full width (in radians) of the peak at half maximum (FWHM) intensity. The value of G was confirmed by using the U-fit program.

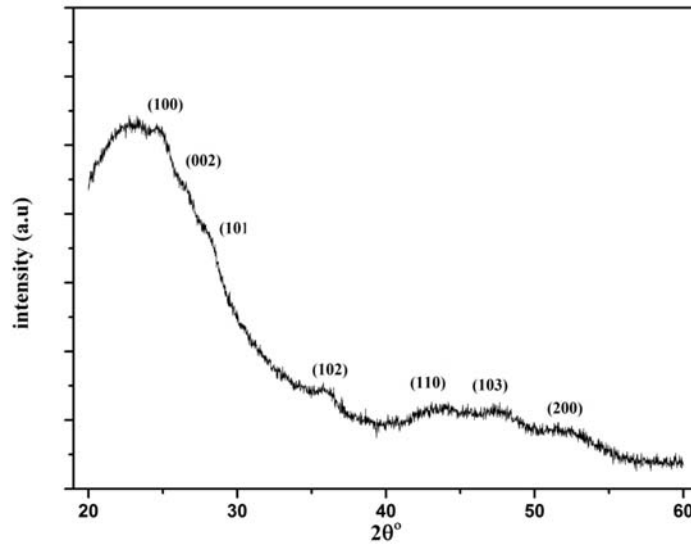
The spectrophotometer Model V-570 UV/VIS/NIR was used to measure the transmittance and the absorption spectrum. The instrument specified by resolution 0.1 nm and wavelength accuracy  $\pm 0.3$  nm (at a spectral bandwidth of 0.5 nm) in the (UV/VIS region).



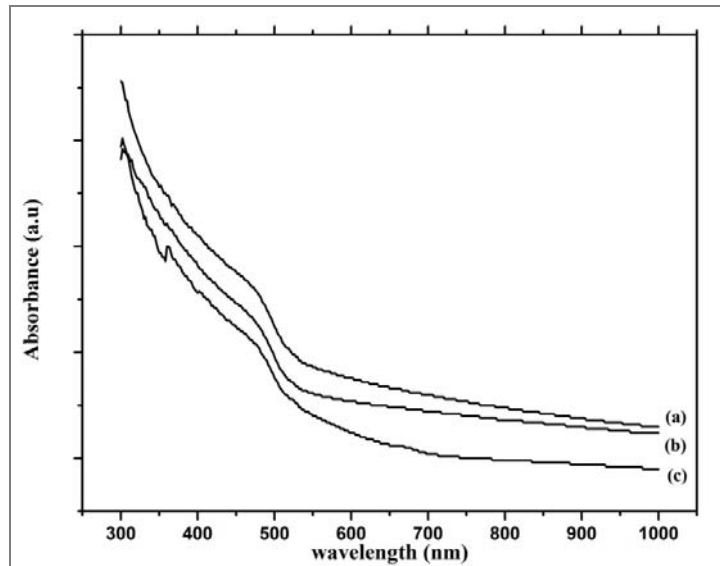
**Fig. 1:** Flow chart for the preparation of Nano-composite silica gel incorporated with CdS in thin film (SCTF) forms.

**Results:**

Fig.2. shows the XRD patterns of the S5C prepared in thin film form, annealed at 400° C for one hour. The peaks centered at 24.92, 26.66, 28.33, 33, 36.82, 43.9, 48.11 and 52.22° corresponding to (100), (002), (101), (102), (110), (103) and (112) planes were appeared in the XRD pattern in the 2 theta range between 20 and 60°.



**Fig. 2:** XRD patterns of (S5CTF) prepared in thin film form, sintered at 400° C for one hour.



**Fig. 3:** Absorption spectra of S5CTF sintered at 200° C (a), 300 (b) and 400° C (c) for one hour, prepared by spin coating sol gel technique.

Fig. 4. Shows Typical plots of  $(\alpha h \nu)^2$  vs  $h\nu$  for S5CTF, annealed at 200, 300 and 400° C. Using the value of band gap estimated from absorption coefficient data as shown in Fig. 4 and substituting in equation 3 we can calculate the particle size for all samples and summarizing the result of band gap and corresponding particle size in Table 1.

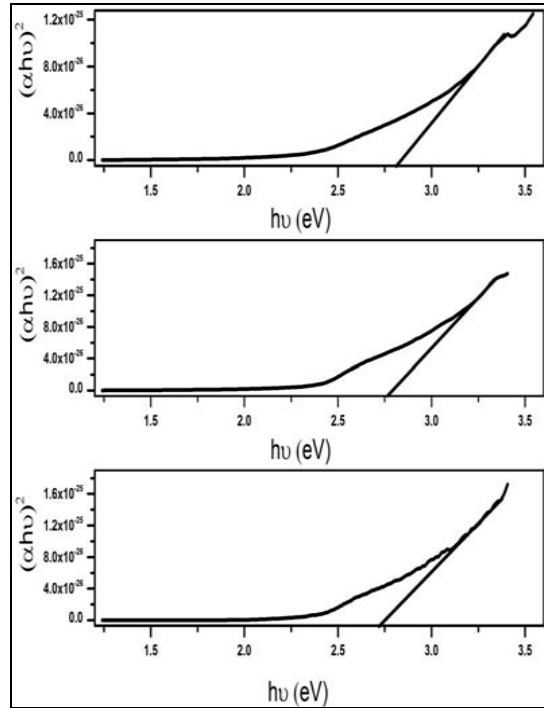
The surface morphology of the prepared S5CTF annealed at 250° C for 1 hour prepared by spin coating sol gel method was shown in Fig.5.

**Discussion:**

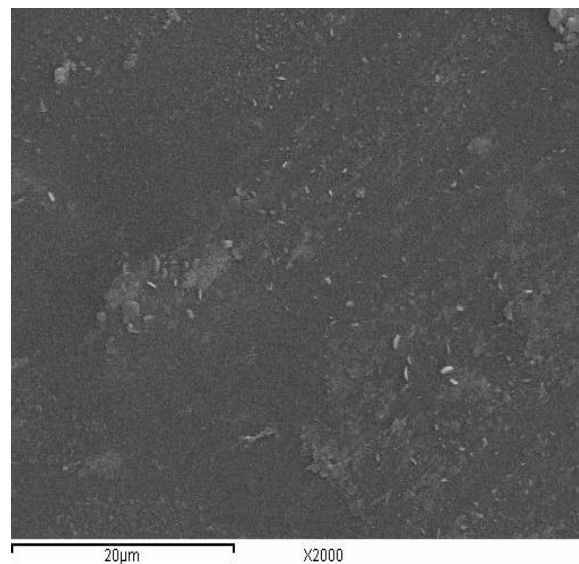
Fig.2. shows the XRD patterns of the S5C prepared in thin film form, annealed at constant temperature 400° C for one hour.

The peaks centered at 24.92, 26.66, 28.33, 33, 36.82, 43.9, 48.11 and 52.22° corresponding to (100), (002), (101), (102), (110), (103) and (112) planes were appeared. The XRD data for S5CTF sample are completely matched with the JCPDS file number (80-0006).

The presence of the mentioned peaks might be due to the presence of the hexagonal wurtzite CdS phase. All peaks were broad indicating very fine crystallite sizes of CdS embedded in amorphous thin film silica gel prepared sample.



**Fig. 4:** Typical plots of  $(\alpha h\nu)^2$  as a function of eV for S5CTF, annealed at 200 (up), 300 (middle) and 400°C (down).



**Fig. 5:** SEM micrograph for S5CTF annealed at 200°C for 1 hour.

Fig. 3. shows the UV absorption spectra for S5CTF annealed for one hour at three different temperature, 200°C (a), 300°C (b) and 400°C (c) respectively.

It is clearly seen from the spectra that, the first absorption peak appeared for the three samples at 464, 474 and 478 nm for 200, 300 and 400°C, respectively.

It is clear from the optical absorption spectra that the absorption edge exhibited a blue shift by decreasing the annealing temperature revealing a characteristic confinement effect on the carriers, due to the reduction of the particle size down to the nanometric scale. This energy shift was reciprocally proportional to the radius indicating a quantum-size effect by decreasing the particle radius for the silica gel containing CdS prepared by the sol-gel process.

By increasing the annealing temperature from 200 up to 400°C the intensity of absorption peaks decreased.

The optical band gap has been estimated from absorption coefficient data as a function of wavelength by using Tauc Relation (Morita *et al.* 2007; Winter *et al.* 2005; Ethayaraja *et al.* 2007; Sahay *et al.* 2007).

$$\alpha h\nu = B (h\nu - E_{np})^n \tag{1}$$

where  $\alpha$  is the absorption coefficient,  $h\nu$  is the photon energy,  $B$  is band tailing parameter,  $E_{np}$  the optical band gap of the nanoparticle, and  $n = 1/2$  for direct band gap and  $n = 2$  for indirect band gap.

The absorption coefficient ( $\alpha$ ), at the corresponding wavelengths, was calculated using the Beer-Lambert's relation (Sahay 2007)

$$\alpha = \frac{2.303 A}{l} \tag{2}$$

where  $l$  is the path length and  $A$  is the absorbance.

It is well known that CdS is a direct band gap semiconductor so  $n = 0.5$  in equation 1. consequently the band gap value was estimated from the plots of  $(\alpha h\nu)^2$  versus  $h\nu$  and extrapolating the straight portion of the graph to  $h\nu$  axis i.e. at  $\alpha = 0$  as shown in Fig. 4.

The size of semiconductor nanoparticles can be estimated by applying Brus effective mass model in strong confinement region (Brus 1984; Dutta *et al.* 2009).

$$E_{np} = E_g + \frac{h^2}{8R^2} \left[ \frac{1}{m_e^*} + \frac{1}{m_h^*} \right] - \frac{1.8e^2}{4\pi\epsilon_o\epsilon R} \tag{3}$$

where  $E_{np}$  is estimated from absorption coefficient data as shown above,  $E_g$  is bulk band gap (2.42 eV for CdS),  $h$  is Planck's constant,  $R$  is radius of nanoparticle,  $m_e^*$  the effective mass of the electro  $m_e$  is the free electron mass (kg),  $n$  (0.19  $m_e$  for CdS),  $m_h^*$  the effective mass of the hole (0.8  $m_e$  for CdS),  $e$  is the electronic charge (C),  $\epsilon$  is the dielectric constant of nanoparticle (5.7 for CdS), and  $\epsilon_o$  is the dielectric constant of vacuum ( $C^2 J^{-1} M^{-1}$ ).

Using the value of bandgap estimated from absorption coefficient data as shown in Fig. 4 and substituting in equation 3 we can calculate the particle size for all samples and summarizing the result of band gap and corresponding particle size in table 1.

**Table 1:** The values of energy band gap and particle radius of S5CTF annealed at different temperature.

Annealing temperature	S5CTF	
	Eg(eV)	R(nm)
200°C	2.81	3.16
300°C	2.78	5.36
400°C	2.71	5.83

From table (1) one can conclude that by decreasing the annealing temperature to 200°C for the incorporated sample with constant molar ration of CdS at 5 mol % (S5CTF), the particle size is decreased. An upward shift in energy is occurred indicating a blue shift attributed to the quantum size effect of the carrier confinement. The energy shift was reciprocally proportional to the radius indicating a quantum-size effect for the silica gel containing CdS prepared by the sol-gel process.

The surface morphology of the prepared S5CTF annealed at 200°C for 1 hour prepared by spin coating sol gel method was shown in Fig. 5. The morphology of the films shows a dense, uniform and homogenous surface with very fine particle size confirming the obtained data from XRD pattern and optical data. The roughness and coarse scale are low in thin film sample annealed at 200°C for one hour and should be caused by closed (bloated) pores directly below the film surface.

**Conclusion:**

Nano-composite silica gel doped with CdS (S5CTF) was successfully prepared by sol-gel technique, using spin coating method. The structure of the prepared samples is evaluated by using XRD. One can conclude that by decreasing the annealing temperature to 200°C for the incorporated sample with constant molar ration of CdS at 5 mol % (S5CTF), the particle size is decreased. An upward shift in energy is occurred indicating a blue shift attributed to the quantum size effect of the carrier confinement. The energy shift was reciprocally proportional to the radius indicating a quantum-size effect for the silica gel containing CdS prepared by the sol-gel process.

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