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Thermal properties of nano crystalline CdS

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Nano CdS samples are synthesized by precipitation method for different growth conditions. Thermal diffusivity and conductivity on these nano CdS are measured by photo acoustic technique. The results are compared with bulk and discussed.

1 Introduction

It is known that nano crystalline semiconductors exhibit quantum confinement and possess the properties intermediate between bulk crystals and molecules. The band gap of these nano semiconductors increases compared to the bulk, giving rise to a blue shift in the absorption spectra [1], influencing the Photoluminescence (PL) and Raman spectra. Most studied nano crystalline semiconductors belong to the II-VI group and among these CdS is one of the most studied materials and efforts are going on to put this into more technological applications. Recently Behera etal [2] have studied the optical properties of the nano CdS in detail, particularly the size dependence on the Raman spectra. They have used an excitation source of 457.9nm Ar laser to observe the Raman spectra for the different nano CdS samples of varying size. In all the cases, a peak at 295cm^{-1} decreases in intensity as the size of the particles increases. This is in confirmity with the surface mode. But when the wavelength of the excitation source is increased (to 488 and 514.5nm) this peak at 295cm^{-1} shifts to high frequency wing, thus rules out it as surface mode. If this 295 cm^{-1} is due to Cd impurities, (this is possible due to excess of Cd in CdS nano system) ,then the intensity should increase when the size of the particles is decreased but should not shift to the high frequency side when the excitation frequency is increased; otherwise there should be a hardening in the force constant. But the measurements of Behera etal show a red shift leading to a softening of force constant. The softening of force constant and broadening of mode on lowering the temperature rules out as an impurity mode.

This type of behaviour has not been reported in literature for any of the II – VI nano systems and so this problem is investigated here with the tool, photoacoustics. Such works and the thermal properties of nano CdS are sparse.

2 Sample preparation

Nano crystalline CdS systems are synthesized from $CdSO_4$, thiourea, NH_4OH, Ethylene Glycol. 0.5M aqueous solution of $CdSO_4$ and thiourea are taken in the ratio 1:1 and NH_4OH is added to maintain the pH at 10.5. By

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precipitation technique, CdS nano particles are collected and they are dried for a day. A known mass of CdS is taken and transformed into pellets by giving different hydraulic pressures. Ethylene Glycol is used to increase the size of the particles as the size dependence of the intensity is planned in this work. The chemical proportions used for the different samples are given below.

(1) $CdSO_4$, NH_4OH and thiourea.
(2) $CdSO_4$, NH_4OH , thiourea and 1 ml of Ethylene glycol (E.G).
(3) $CdSO_4$, NH_4OH , thiourea and 5 ml of Ethylene glycol (E.G).

In each of the above three cases, the powders of CdS on precipitation are collected and subjected to a hydraulic pressure of 1, 2, 3 and 4 tons on separate collections to make different pellets i.e., for each case, there will be 4 different pellets. The size of the nano particles are found out from XRD and Shieber's relation in each case. The size of the present CdS varies from 10 nm to 35 nm (due to the addition of E.G**).** (It is known that a bulk sample will have a particle size more than 75 nm).

3 Photo acoustics

Photo acoustic spectroscopy (PAS) offers minimal or no sample preparation, the ability to look at opaque and scattering samples [3] and the capability to perform depth profiling experiments. In particular, depth profiling experiments are useful for the characterization of surface coated and laminar materials and for studies of weathering, aging, curing, and the diffusion of species into or out of a polymer matrix.

When a modulated light is absorbed by the sample located in a sealed cell, the non radiative decay of the absorbed light produces a modulated transfer of heat to the surface of the sample. This modulated thermal gradient produces pressure waves in the gas inside the cell that can be detected by the attached microphone. The resulting signal depends not only on the amount of heat generated in the sample (and, hence, on the optical absorption coefficient and the light-into-heat conversion efficiency of the sample) but also on how the heat diffuses through the sample [4]. The quantity, which measures the rate of diffusion in a material, is the thermal diffusivity α. Apart from its own intrinsic importance, thermal conductivity can be directly evaluated from this thermal diffusivity.

4 Photo acoustic spectrometer

400 W Xe- lamp (Jobin Yvon) is used as the light source. The sample is placed in the PA cell and the mike is placed very near to the sample. To get the modulated light, a mechanical chopper (Model number PAR 650) is used with the source. The PA signal from the sample is fed to a lock in amplifier (Model Perkin Elmer 7225 DSP). The light is allowed to fall on the sample through a monochromator (Model Triax 180, Jobin Yvon). Before doing the actual experiments, the spectrum profile of Xenon lamp was studied and proper care is taken when the spectral response of the nano system is studied i.e. only in the region where the spectral profile of Xenon is nearly flat, the spectrum for the nano systems were recorded. [Xe lamp will have an emission peak ~ at 480 nm].

5 Depth profile

For measuring the thermal diffusivity of the sample at room temperature, the variation of the PA signal is observed for different chopping frequencies. This is given in Fig.1 as a typical example for the particle size of ~13 nm. For other samples, such figures are not given here. Thermal diffusivity is then calculated from the characteristic frequency of the sample (The characteristic frequency is defined as the frequency at which the sample goes from thermally thick to thermally thin region). The plot of PA amplitude versus chopping frequency (Fig. 1) shows a distinct change in slope at a frequency at which crossover takes place. This is taken as characteristic frequency and is marked in the figure itself.

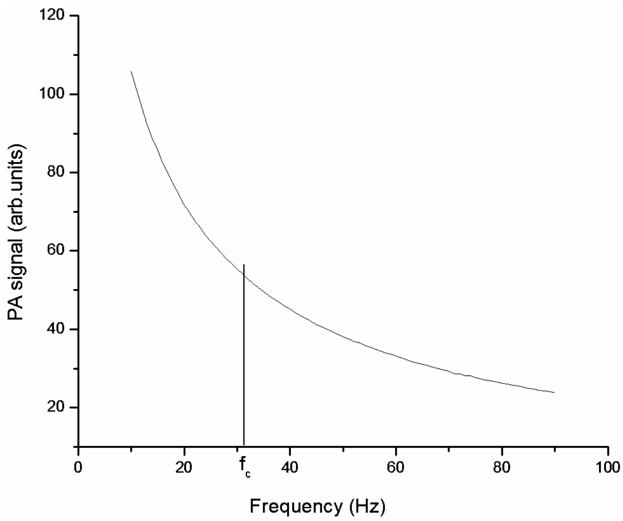

Fig 1 Depth profile analysis for sample 2 of particle size 13 nm.

If f_c is the characteristic frequency of the sample of thickness *l* then the thermal diffusivity can be calculated from,

$$D = f_c l^2 \text{ m}^2/\text{sec} \tag{1}$$

and thermal conductivity from

$$\kappa = D\rho C_p \text{ W/m-K} \tag{2}$$

where ρ is the density and C_p is the specific heat capacity of CdS [5]. The results on these thermal properties are given in Table 1. Similar measurements are done for other samples, (of varying particle sizes) also and the results are given in the same Table 1.

Table 1 (a) Thermal parameters for the nano CdS from photoacoustics, Particle size: 13 nm.

Sample	Chemicals used	Thermal diffusivity (D) x 10^{-5} (m^2/sec)	Thermal conductivity (w/m-k)	D x 10^{-7} (m^2/sec) for bulk CdS	Reference for the bulk D
Sample 1	$CdSO_4$ + thiourea +NH_4OH	3.07	40.8	3.5	[6]
Sample 2		3.21	42.7		
Sample 3		3.48	46.2		
Sample 4		3.77	50.1		

(b) Particle size = 20 nm.

Sample	Chemicals used	Thermal diffusivity (D) x 10^{-5} (m^2/sec)	Thermal conductivity (w/m-k)
Sample 5	$CdSO_4$ + thiourea +NH_4OH+ 1 ml E.G	2.98	39.6
Sample 6		3.02	40.17
Sample 7		3.28	43.6
Sample 8		3.42	45.4

(c) Particle size = 33 nm.

Sample	Chemicals used	Thermal diffusivity (D) x 10^{-5} (m^2/sec)	Thermal conductivity (w/m-k)
Sample 9	$CdSO_4$ + thiourea +NH_4OH+ 5 ml E.G	2.58	34.3
Sample 10		2.83	37.9
Sample 11		3.09	41.1
Sample 12		3.2	42.5

6 Photo acoustic spectrum

Photo acoustic spectrum will be proportional to the absorption of the sample. The PA spectrum of the powdered nano CdS was obtained by recording the PA signal as a function of the wavelength of the incident beam (from 400nm –700nm) for a constant modulation frequency of 20 Hz. The PA spectrum for each sample is normalized using the PA spectrum obtained for air in the allowed region of Xe lamp. Optical absorption coefficient is directly proportional to the PA signal and from the PA amplitude-wavelength plot, shown in Fig 2, the energy gap is determined. The wavelength λ_g, corresponding to the peak in the PA spectrum is measured as 424 nm. From this, the band gap is calculated using the relation $E_0 = hc / \lambda_g$ and the result is given in Table 2. (The energy required to go from valence band to conduction band is energy gap). Similarly, for the other samples, such values for the band gap are measured.

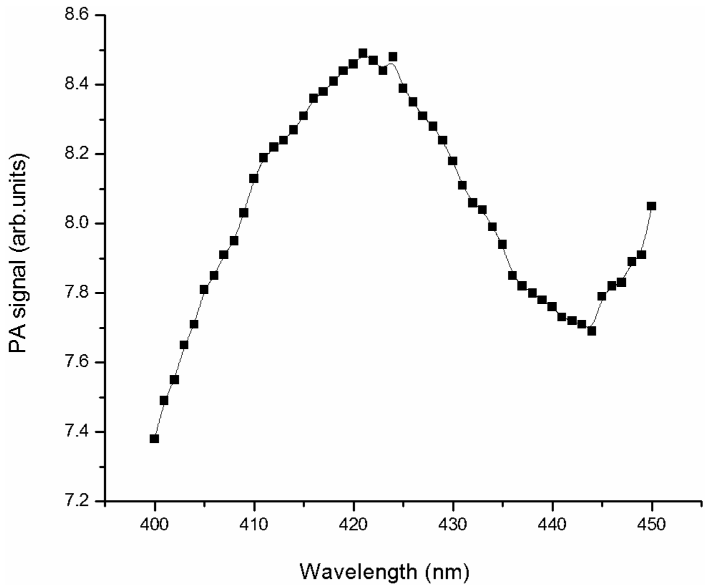

Fig. 2 PA Spectrum for the sample 2 of particle size – 13 nm.

7 Results and discussions

In Table 1, the variations of thermal parameters are given in terms of the sizes. The size of the nano particles depends on the amount of EG added. It is clearly seen when the size of the nano particles increases (as EG amount increases), the amplitude of PA signal decreases and hence the thermal diffusivity and thermal conductivity. That is as the size increases the thermal properties decreases approaching the bulk value. This shows that the thermal properties of the nano CdS will be higher by at least two orders of magnitude than the bulk value as given in Table 1 [6].

Behera et al. have found that as size increases there is a dramatic shift of 295 cm^{-1} towards high frequency, disqualifying as a surface mode when the excitation frequency is increased. If it is a localized mode, there should be an increase in the force constant whereas softening is reported. This result is now analysed with respect to our PA measurements. Our results are in contrast with the expectation of Behera etal that there is decrease in the thermal property here, as the size of the particle increases. Decrease in thermal diffusivity or thermal conductivity, is due to the decrease in the population of phonons. Otherwise more phonons are not generated and hence less scattering. This is possible when there is an increase in force constant.

For example, the effects of the particle size on the magnetic and transport properties in nano $La_{0.875}$ $Sr_{0.125}$ MnO_3 have been studied by Anulekha et al. [7]. They have varied the size of the particle from 18nm to 50nm. Even though there is no signature of structural transitions compared to the bulk and single crystalline samples, large changes in the resistivity are observed for nano systems. For example, the metal – insulator transition temperature for particle size of 50 nm is 112 K whereas for particle size of 18 nm this is 170 K i.e., as the size goes larger, this goes towards the bulk value.

Similarly, Anulekha et al [7] have made measurements on transport properties in nano $LaSrMn0_3$ and reported about 4 to 6 orders of magnitudes higher for nanosystems than bulk.

Horvak et al. [8] have studied Cu diffusion in a nano crystalline material is expected to be comparable or even higher in the rapid short circuit diffusion along grain boundaries. Because of the small size of the particles, the interfaces may form an extermly dense network of paths for fast diffusion through the nano crystalline material. Horvak etal [8] for the first time made diffusivity (D) measurements on nano crystalline copper, by radio tracer technique.^{67} Cu was used for the study of self diffusion in nano Cu. The temperature dependence of D in the small temperature interval covered in this study may be described by an Arrhenius law,

$$D(T) = D_o \exp(-H / KT) \tag{3}$$

D_0 is the pre exponential factor which is the temperature independent diffusion constant and H the activation enthalpy for the diffusion in the interfaces.

The results show that the diffusivity in this nano copper system is about 16 orders of magnitude larger than the bulk diffusion. This is shown here because the transport properties in nano systems is more rapid than the bulk system.

Here we report the results on the thermal properties of the nano crystalline CdS, synthesized from chemical route, by photo acoustic (PA) spectroscopy, where the effect of size dependence is analyzed and compared with bulk and the other available experimental results.

This study on nano CdS by photo acoustics for thermal diffusion shows at least two orders of magnitude higher than the bulk CdS. Also, as the size of the particle increases, this is going towards the bulk value, i.e the transport is slowed down.

Similarly, the band gap from the present measurements is 2.92 eV. This agrees with the UV-VIS measurements of Behera et al. On the other hand, there is a marked increase of about 0.5 eV from the bulk value of 2.405 eV. From the optical absorption study, the band gap of bulk CdS of average size 90nm is found to be 2.41eV as given in Table 2 [9].

Table 2 Band gap for nano CdS.

Author		Optical band gap (eV)	Reference
Present work	Nano CdS* (size = 13nm)	2.92	_
Behera et al.	Nano CdS (size = 10 nm)	2.97	[2]
Gal et al.	Bulk CdS (size = 90 nm)	2.41	[9]

* experimental error = 2 %

This has been theoretically verified from the known equation,

$$E_{gn} = \left[E_{gb}^2 + \left\{ \frac{2h^2 E_{gb} \left(\frac{\pi}{R} \right)^2}{m^*} \right\} \right]^{1/2} \tag{4}$$

where, E_{gb} is band gap of bulk semiconductor (2.405eV for CdS), R is the particle radius, m* is the effective mass of the electron and E_{gn} is the band gap for the nano system. ($\frac{m^*}{m_e}$ = 0.2 for CdS [10] where m_e is the mass of free electron).

The energy gap corresponding to the peak at 424 nm is 2.92 eV from the present measurement of Fig.3. It is used as E_{gb} in equation (4) to calculate the particle size R. This has been verified by XRD measurements also.

The width of the XRD peak can be directly related to the particle size, by Shieber's equation and with that the particle size is estimated. These measurements on the band gap by PA show that the particle size will have a control over the band gap. The immediate application is, LEDs of different colors can be designed with nano CdS at ease, by manuoring the particle size.

Another interesting result could be seen in Table 1 (a), (b) and (c). For a particular size of the particles (average size), the pellets are formed by applying different pressures. As the pressure (applied) increases, there is a uniform increase in the thermal diffusivity of the nano CdS. This is because when the pressure is applied, there are changes in the connectivity of particles. This in turn increases the strength of the PA signal and hence the thermal diffusivity. This is verified for the varying particle sizes and pressures. In all the cases, as seen from Tables 1, this is clearly seen and such a result has not been reported for nano CdS in the literature.

Finally, it is concluded here that the thermal diffusivity will increase with the decrease in particle size in CdS and it would be better to apply pressures on these nano particles to have good connectivity so that the measurements will be much pronounced

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