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On the phase transformation of CdS to $CdCO_3$ by photoacoustics

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The results of Portillo et al. (Superfices y Vacío 15, 19-21,2002) on the phase transition in CdS are analysed entirely by a different route here. With CdS single crystal taken in wafer form, photoacoustic measurements are carried out in the presence of carbon and air. Phase transformation from CdS to $CdCO_3$ is obtained at a temperature of 80^0 C which agrees well with the results of Portillo et al.

Keywords: Photoacoustic spectroscopy (PAS); CdS; Thermal diffusivity

1. Introduction

Phase transition from CdS to $CdCO_3$ (hexagonal), when thin films of $CdCO_3$ was attempted (and in fact this happens to be the first ever report on the growth of cadmium carbonate thin film) by chemical bath (CB) method was recently reported by Portillo et al [1] They have actually synthesized CdS by chemical bath method by taking $CdCl_2$, KOH, NH_4NO_3 and $SC(NH_2)_2$ solutions mixed at equal volume proportion to have a pH of 8.3. When this solution is heated from ambient to about 120^0C at different temperatures and deposited on a glass substrate, different samples are obtained. For these samples the XRD and optical absorption spectra measurements are made to find that below 80^0C, it is a mixed phase of CdS and $CdCO_3$ and above 80^0C it is purely CdS. ie they have observed that between 23 –80^0 C, there will be an intermediate phase between CdS and $CdCO_3$ and at 80^0 C, the zinc blende CdS is exclusively seen. ie $CdCO_3$ was predominant in the layer at 23^0C whereas it is CdS at 80^0C. ie a phase transformation was observed at temperature of 80^0C where zinc blende CdS becomes stable. This is an interesting case of phase transition. This transition is identified from the physical properties of the film by means of XRD and optical absorption methods.The energy band gap of this direct transition was also worked out to confirm this transition.

For systems like CdS or $CdCO_3$ the melting points are so high that a transition at 80^0C is quite unusual. So this needs a detailed investigation to find whether S is replaced by CO_3. Here we report our study on CdS crystal in the presence of carbon by photoacoustic (PA) measurements which has successfully been applied for the phase transformation of the sample.

2. Experiment

Here, we do not synthesize the films as done by Portillo etal but we make measurements with CdS single crystal. Physical vapour transport technique is used to grow the CdS crystals and the details of the growth are already given[2]. Good single bulk crystals in cm size are obtained with high purity. Crystalline nature and electrical properties are also already reported[2]. Wafers of thickness less than 0.1 mm are sliced from the as grown samples and polished with 10% of bromine in ethyl alcohol for about 2 minutes. The crystals are cleaved along the (110) faces with the thickness of the sample in few micrometres. These are used for the PA measurement. The present PA spectrometer used for the study of phase transition is set up with a Xenon lamp (450 Watts), monochromator (100-1000nm, Jobin Yvon), mechanical chopper (PAR), photoacoustic cell, a condenser mike, a lock in amplifier (PAR DSP 7225) for amplifying the PA signal by which the amplitude and phase of the signal are measured.

We have fabricated the heating compartment using nichrome (28 gage) wire as heating element fixed with plaster of paris around the PA cell to vary the temperature of the sample. The PA cell is made up of stainless steel. It is present inside the cylindrical container of length about 0.5 metre.The microphone compartment carrying the condenser mike is attached to the container by another rod of length nearly 10cm and very narrow diameter. It is sealed well with a bad conductor so that more heat cannot be transmitted into the microphone. Thus it is isolated from the heating element to avoid direct heating of the condenser mike which detects the PA signal. The temperature can be varied up to 300^0C and Al-Cr thermocouple is used to measure the temperature . This is digitally observed in ^{0}C with an accuracy of 1^0C. This set up is first calibrated with an accurate thermometer for different temperatures. Then

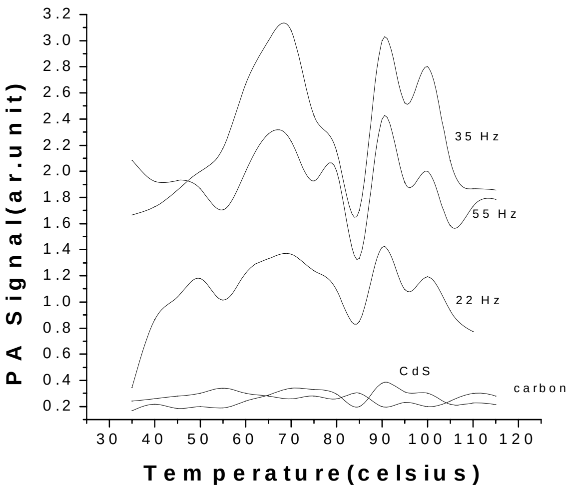

Figure 1a. Temperature Vs PA signal for CdS.

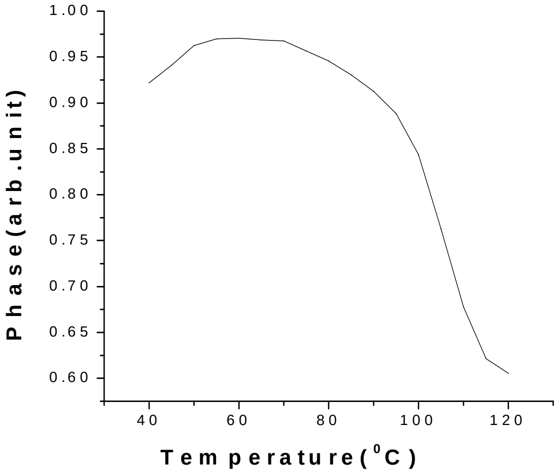

Figure 1b. Temperature Vs Phase.

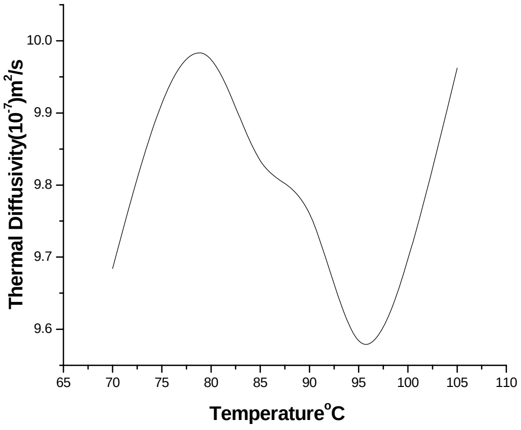

Fig 1c. Temperature Vs Thermal diffusivity.

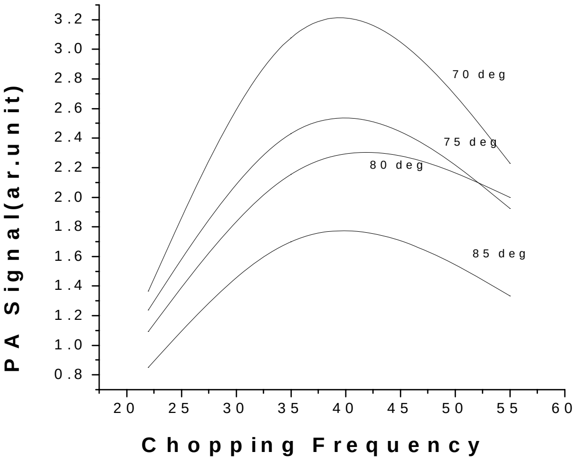

Figure 1d. Frequency Vs PA signal.

only the PA measurements for the CdS system for various temperatures are observed.

The crystal is then introduced in the PA cell and very close to the sample a piece of carbon is placed as a backing material. In general, when PA measurements are done, the thermal properties of the backing material should not affect the thermal properties of the sample. But here , we have deliberately used carbon as the backing material so that on heating whether there is any possibility for the carbon atoms to get transported into CdS to form $CdCO_3$(as there is always oxygen present in the PA cell). The temperature is varied from the ambient to the maximum of 120^0C in steps of 5^0 C.

3. Measurements

The beam of white light from Xenon lamp is chopped at an audio frequency of 22 Hz. This frequency is chosen here from the previous works on CdS crystal [2] and is the characteristic frequency of the sample. It is then allowed to fall on the sample which is mounted inside the airtight PA cell. The periodic absorption of energy by the sample results in the heating of the air medium and generates a sound wave at the chopping frequency. This is detected by the mike and fed to the digital storage oscilloscope (DSO GOULD 20 MHz) and lock in amplifier. The variation of PA amplitude with the temperature has been measured and recorded as shown in Fig.1a. This is repeated again for two more chopped frequencies of 35 Hz and 55 Hz. Similarly the variation of phase with temperature also has been measured and recorded as shown in Fig.1b. In both the observations (Fig 1a &1b), the PA amplitude first increases with the temperature and starts to decrease at a temperature around 80^0C.

The reason for this was analysed to find transport of carbon into the sample CdS to form $CdCO_3$ due to the oxygen present in the PA cell as the CdS crystal grown is enriched with Cd concentration. As we have mentioned earlier, this possibility is rare when the melting points of CdS or $CdCO_3$ are considered.

Table.1 Variation of thermal diffusivity with temperature.

Temperature (^{0}C)	**Thermal diffusivity** ($10^{-7}m^2/s$)	**CdS** ($10^{-7}m^2/s$)
70	9.69	
75	9 .91	Ref(2)
80	9.97	at 300 K
85	9.83	3.57
90	9.76	
95	9.58	
100	9.70	
105	9.96	

But Shivrin etal [3] have reported some interesting results as early as in 1989 when they studied the mechanism of oxidation of metal sulphides like CdS, ZnS,In_2S_2 etc by water vapour method and have found that the oxidation begins at a temperature $\geq$ 0.3285 T_b where T_b is the boiling point of metal in metal sulphide. The boiling point of metal ie Cd in CdS is 1050 K and so the oxidation at about 350 K (85^{0}C) is expected from the empirical relation proposed by Shivrin etal.

Now, our measurements also show a drastic change at 85^{0}C. Therefore the formation of $CdCO_3$ cannot be completely ruled out at intermediate temperatures.This decreases the PA amplitude after 80^{0}C showing a transition from CdS to $CdCO_3$ and thus the phase of $CdCO_3$ is maintained at 80^{0}C. This has been further verified from the variation of phase measurements with temperature as shown in Fig.1b.

Here again, the phase of the signal is found to increase first and at a particular temperature of 80^{0}C, it remained constant. Thereafter it starts to decrease as the temperature increases. This shows that this is the temperature at which the zinc blende phase of CdS is maintained from the hexagonal (rhombohedral) phase of $CdCO_3$. By this way, we have demonstrated the Xray diffraction measurements of Portillo etal proposing the growth of $CdCO_3$ from CdS. ie For example,

$$2Cd^{2+} + O_2 \longrightarrow 2CdO \text{ (at } 80^0\text{C)} \quad (1)$$

Since the carbon is the backing material,

$$2CdO + 2O_2 + 3C \longrightarrow 2CdCO_3 + C \quad (2)$$

So, there is a possibility to going from CdS to $CdCO_3$ and this $CdCO_3$ is not very stable.

In general, the PA signal is proportional to $(\mu/T)(2\rho C_s)$ i.e it is inversely proportional to the temperature. Now if we look at Fig:1a, we see there is an increase first and then only at about 80^0 C there is a decrease as expected. Thermal diffusivity is also worked out from PA measurements for various temperatures in this region and the variation of diffusivity as a function of temperature is shown in Fig.1c. It increases first and at around 80^{0}C, it starts to decrease which shows that there is a change in the thermal property following the theory of Rosencwaig Garsho(RG) [4]. According to this theory, the PA signal will vary as 1/f, where f is the chopping frequency, in the thermally thin region. Moreover the equation used to calculate the thermal diffusivity is valid only in the thermally thin region. The equation is given below:

$\alpha = f_c\, l^2$

where 'l' is the thickness of the sample and α is the thermal diffusivity.μ, ρ, C_s are the diffusion length, density and specific capacity of the sample respectively. The characteristic frequency f_{ch} of CdS at 80^{0}C is 39 Hz and the thermal diffusivity is increased atleast by a factor of 3 compared to the ambient value as shown in the Table 1. This is also an useful result as the thermal properties are affected in any transition.

4. Results and discussion

The present method of measurements is completely different from the works of Portillo etal, starting from the preparation of the sample. Here CdS single crystals were grown by PVT method and for photoacoustic measurements, this sample was cleaved into thin wafers (of thickness l_s =70 μ m). This is very essential for this particular experiment, as thermal diffusion length of CdS is 90 μ m from literature. Now when we place this CdS along with another carbon wafer which is again about 100 μ m, in a sandwiched form (not glued) for the backing material, the heat energy diffused into the sample CdS can reach the carbon black, as $\mu > l_s$. Since CdS will absorb all the light energy, this will heat up the carbon wafer. As both CdS crystal and carbon black are in wafer forms, we expect the light energy to interact with carbon.

Now the reactions given in equations (1&2) would take place to form $CdCO_3$, thus leading to phase transition. This way, the experiment is totally different with the experiment of Portillo etal. The present PA measurements and that of Portillo et al reveal one important point that there is a transformation at about 80^{0}C. Eventhough our PA measurements agree with the Portillo etal,it is interesting to see such a transformation at this temperature, as the melting point of Cd and C are very high. This is now explained here on the basis of the work of Shivrin etal.

Shivrin etal [3] have reported that the composition of reaction products was dependent on temperature and the H atom in the water vapour can combine (reduction) with the sulphur in CdS and this has also been observed but at lower temperature. ie. it is clear from this experiment, oxidation is possible in CdS at temperature ≥ 0.3285 T_b and reduction at low temperature. In the present PA experiment we have CdS and carbon apart from the air medium that is present in the PA cell. Therefore if we extend the concept of Shivrin etal, here the oxygen is available(from the air medium) to undergo oxidation process, at around 85^0C. ie the Cd atoms on the surface of the sample undergo oxidation at this temperature to form CdO first. This is understood from shivrin and from our measurements at 85^0C. But the chance of transforming to $CdCO_3$ is not confirmed by this. But the thermal diffusivity measurement above 85^0C is very near to $CdCO_3$ and so it is concluded that the cadmium oxide from the CdS sample can get into the carbon black to form $CdCO_3$. For example we removed the carbon black and repeated the same experiment, where the results are not in this range for thermal diffusivity. All these confirm such transformation between CdS and $CdCO_3$.

The present PA measurement shows this possibility of transport of carbon at temperature above 0.33 T_b approximately. ie. The CdS backed with carbon black when oxidized there is a possibility of $CdCO_3$ at 80^0C. We expect CdS and carbon exist separately at lower temperature below 80^0C. This is also seen in Fig.1d where the variation of the PA signal with chopping frequency for very close temperatures is shown. We found unusual trend at 80^0C in the observations, as there is a cross over at 80^0C in this Fig.1d with the other temperature of 75^0C. The other curves at 70,75 and 85 all show uniform trend except this at 80^0. As there is an intersection between 75^0C and 80^0C, the mixed phase at this temperature is visually seen.

Similarly in Table.1, as the temperature increases from 70^0C there is an increase in thermal diffusivity whereas at 80^0C, this value begins to decrease. This means that there is an additional mass transport has taken place in CdS.

But Portillo etal started with $CdCO_3$ and CdS as two separate layers sandwiched and they have found the transition at 80^0C, going completely into CdS phase. ie to start with there is a mixed phase of $CdCO_3$ and CdS but at 80^0C, there is only one phase of CdS. Here we have not started with two layers of $CdCO_3$ and CdS but kept carbon very close to CdS with oxygen present. There is an unusual behaviour at 80^0C in our present case also, eventhough it is not a permanent change. It is reversible here also as seen by Portillo etal. ie during the fall of temperature, thermal diffusivity decreases to around $3.6\text{x } 10^{-7}m^2/s$ at room temperature, which is nothing but the value of thermal diffusivity of CdS at room temperature. ie CdS and $CdCO_3$ can be seen in our present experiment also.

This photoacoustic measurements could reveal the possibility of mass transport in CdS which would otherwise be difficult to measure by other conventional techniques.Here thermal diffusivity of CdS under various temperatures has been worked out from PA measurements and the change in this thermal property at 85^0C clearly indicates the transition in the presence of carbon.. The value ($9.97\text{x}10^{-7}m^2/s$) is also not that of bulk CdS (which is $3.6\text{x}10^{-7}m^2/s$) and so the diffusivity is essentially due to the formation of $CdCO_3$.

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