Research Paper

Synthesis and Characterization of Cadmium Sulfide Crystals Grown by DVT Technique

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Abstract: Cadmium Sulfide crystals were grown by direct vapor transport (DVT) from high-purity starting materials. The grown CdS crystals were orange in color, transparent, dendrite platelets shaped were observed. The structure of CdS crystals has been studied with the help of X-ray diffraction (XRD) and Transmission Electron Microscope (TEM). The crystals grown by DVT technique possess hexagonal structure. The morphology of the surface of the grown crystals was studied by the optical micrograph and the Scanning Electron Microscopy (SEM). The direct energy bandgap has been estimated from the absorption coefficient values using Tauc’s procedure which is found to be 2.37 eV.

Keywords: Growth from vapor, SEM, XRD, TEM, Optical absorption.

1. Introduction:

Cadmium sulfide (CdS) is one of the most important members of the metal chalcogenide family. It exists as two different polymorphs, hexagonal (wurtzite) form or cubic (zincblende) form, or mixture from them depending upon the thermodynamic parameters and growth techniques but wurtzite is the common form of CdS with a band gap of 2.4 eV[1-3]. Therefore, it was playing an important role in opto- electronic devices such as multilayer light emitting diodes, phototransistors, the window layer in hetero- junction solar cells and so on[4-9]. A variety of defects occur in semiconductor crystals, many of which lead to degradations in performance and require careful growth and fabrication conditions to minimize their occurrence [10]. According to this fact, the selection of growth method plays an important role in the quality of grown crystals. Many kinds of crystal growth techniques have been developed for various compound semiconductor including grown CdS crystals like bridgeman and sol-gel methods, direct vapor transport (DVT), chemical vapor transport (CVT), Flux
growth Technique etc.[11-15]. Among these, direct vapor transport (DVT) has been used in the present study to reduce the density of dislocations and other growth defects because of the advantage of low-temperature growth [13-15].

2. Experimental:

Crystals of CdS were grown by direct vapor transport (DVT) method inside a dual zone horizontal furnace. High pure powder of Cd (99.99 % pure) and S (99.99 % pure) was used as starting material. The ampoule containing the source material was to be evacuated to a pressure of $10^{-5}$Torr to minimize the reaction of the elements with atmosphere at elevated temperatures to get a high purity final product. Proper care was taken while evacuating the ampoule so that material from ampoule does not enter into the vacuum system. Once the vacuum of $10^{-5}$Torr was reached, the loaded ampoule was sealed off at the construction of the 8mm of inner diameter quartz tube. Growth and source zone temperatures were 930°C and 980°C respectively and the time duration of growing CdS crystals was about 168 hours with cooling rate about 5°C/h. The experimental setup of a dual zone horizontal furnace shown in figure 1. The optical micrographs of as grown surfaces of the crystals as well as photographic recording of the observations have accomplished with the help of Axiotech 100 reflected light microscope, manufactured by Carl Zeiss Jena, Germany. To get a clear picture of crystal surfaces, scanning electron microscopy (SEM) of CdS crystals was carried out. The X-ray diffractogram (XRD) of CdS was recorded with the Philips X Pert MPD diffractometer to verify the phase and crystallinity of the compound. In order to record the X-ray spectrum of the sample, synthesized product was crushed homogeneously with the help of mortar and pestle. The hkl reflections of the grown crystals were determined by comparison d spacing with JCPDS data. Also, the lattice parameters a, c and volume were obtained from the diffractogram of CdS and transmission electron microscope (TEM) characterization has been carried out also. The optical properties of as grown CdS crystals were studied at a wavelength range of 200–1200nm at room temperature using the UV-VIS-NIR spectrophotometer (Perkin Elmer-USA, Model: Lambda 19).

![Figure 1: Experimental arrangement of a dual zone horizontal furnace](image-url)
3. Results and Discussion:

These crystals were in the form of thin platelets shaped with the presence of dendrite on the growing faces, orange in color and smooth in appearance. The average crystal dimensions were 3-10 mm$^2$ in cross sectional area and few micrometers in thickness (see figure 2).

![Figure 2: CdS crystals as grown by (DVT) method](image)

3.1 Optical Micrograph:

The crystals grown were examined under an optical microscope which indicates spirals on the grown faces of these crystals, that suggests a screw dislocation mechanism of the grown crystals as shown in figure 3(a). In figure 3(b), multi-layer CdS surface were observed in the form of flat platelet whose area increases much more rapidly than its thickness. Furthermore, figure 3(c) shows a hexagonal shape with etched surface.

![Figure 3 (a-c): A micrograph features on the grown surface of CdS crystals](image)
3.2 SEM:

SEM images were taken at different magnification for CdS crystal as shown in figure 4 (a, b and c). Figure 4(a) indicates that hexagonal crystal of CdS which was separately grown with dimensions $\sim 317 \mu m \times 382 \mu m$. Figure 4(b) confirms the multi-layer growth of crystals and figure 4(c) shows the stepwise growth of hexagonal structure inside the crystal surface. Furthermore, the dimensions of growing crystals varies from 82.8µm to 548µm can be seen from the randomly labeled SEM images as shown in figure 4(a, b and c).

![SEM micrograph of CdS crystal at different magnification](image)

Figure 4 (a-c): SEM micrograph of CdS crystal at different magnification

3.3 X-Ray Diffraction:

Figure 5 shows the X-ray diffractogram of CdS crystal grown by direct vapor transport (DVT) method. The comparison of experimentally observed d-spacings of CdS crystals with JCPDS data confirms that grown crystals were of CdS and possess hexagonal (polycrystalline) structure and in good agreement with JCPDS data for CdS. The values of lattice parameters for CdS crystals in present investigation were in good agreement with that reported in the JCPDS and earlier reported data [16, 17] were presented in table 1. The average grain sizes have been determined by using the Scherrer formula [18]:

$$d = \frac{0.9 \lambda}{\beta \cos \theta}$$  \hspace{1cm} (3.1)
Where \( \theta \) is the diffraction angle, \( \lambda \) is the wavelength of the X-ray source (\( \lambda = 1.54056 \) Å) and \( \beta \) is measured in radians as full-width at half maximum of the diffraction line.

The average grain size of CdS crystallites was found to be about 296nm. The average microstrain (\( \varepsilon \)) for CdS crystallites were evaluated using the equations (3.2) given below. It’s found to be about 1.3\( \times 10^{-3} \) m\(^{-2}\).

\[
s = \frac{\beta 2 \theta \cos \theta}{4}
\]  

(3.2)

The value of the dislocation density (\( \delta \)) which is related to the number of defects in the crystal was calculated from the average values of the grain size (‘t’) by the relationship (3.3) given below, it’s found to be about 1.23\( \times 10^{15} \) m\(^{-2}\).

\[
\delta = \frac{1}{t^2}
\]  

(3.3)

The lattice constant ‘a’ and ‘c’ have been determined from interplanar spacing of different (hkl) planes using the relation (3.4)

\[
\frac{1}{d^2} = \frac{4}{3} \left( \frac{k^2 + h^2 + l^2}{a^2} \right) + \frac{l^2}{c^2}
\]  

(3.4)

The calculated values are in good agreement with that reported in the JCPDS. Using the values of lattice parameters a, c the unit cell volume has been calculated with the help of the equation (3.5):

\[
V = \frac{\sqrt{3}}{2} c^2 a
\]  

(3.5)
**Table 1:** Observed and reported lattice parameters of CdS crystals used in the present investigation

<table>
<thead>
<tr>
<th>Lattice Parameters</th>
<th>a(Å)</th>
<th>c(Å)</th>
<th>V(Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS Crystal</td>
<td>4.125</td>
<td>6.720</td>
<td>98.955</td>
</tr>
<tr>
<td>Reported (JCPDS)</td>
<td>4.136</td>
<td>6.713</td>
<td>99.450</td>
</tr>
</tbody>
</table>

3.4 TEM:

A typical electron diffraction pattern of CdS crystals was shown in figure 6. The spacing and corresponding (h k l) planes for all rings in the diffraction patterns were calculated by using equation (3.6):

\[ d = \frac{2\lambda L}{D} \]  

(3.6)

Here D is the diameter of the rings, 'L' is the distance between photographic film and the specimen, and 'λ' is the wavelength of the electron beam. The selected-area electron diffraction (SAED) pattern shows rings indexing as (002), (102), (110), (112) and (300) planes. The XRD and SAED diffractions give hexagonal crystalline and these results were in good agreement with standard JCPDS data [17].

![Electron diffraction patterns for crystalline CdS.](image)

**Figure 6:** Electron diffraction patterns for crystalline CdS.

3.5. Absorption Spectra:

The optical spectra of as grown CdS crystal have been recorded in the range 200-1200nm as shown in figure 7. The result of this investigation has been used for the calculation of the energy band gap of grown crystal with the help of Tauc relation [19]:

![Optical spectra of as grown CdS crystal.](image)
\[ \alpha h \nu = A( h \nu - E_g)^r \]  \hspace{1cm} (3.7)

Where, \( A \) is a constants, \( \alpha \) is the absorption coefficient, \( h \) is Planck’s constant and \( \nu \) is the frequency of the radiation, \( r = 1/2 \) for a direct band gap material. In light of this, the value of the energy band gap was estimated from the intercept of the straight line of \((\alpha h \nu)^2\) versus \((h \nu)\) shown in Figure 8. It’s found to be about \( E_g = 2.37\) eV.

![Figure 7: The optical absorption spectra of CdS grown by DVT.](image1)

![Figure 8: The energy band gap for CdS crystal](image2)
The reduction in the value of the measured band gap are mostly due to strongly depend on the growth conditions and the reflection from defect centers in the different grown crystals, that is might be reason of reduce the band gap of the cadmium sulfide [20].

4. Conclusions:

The direct vapor transport technique could be successfully used to grow the CdS crystal in hexagonal form. The presence of dendritic platelet crystals is observed may be due to high cooling rate. It is common observation that CdS crystals having multilayer growth conforms from optical micrographs and SEM images. Furthermore, d-spacing obtained from X-ray diffraction conforms the presence of hexagonal phase of crystal structure also transmission electron microscopy (TEM) gives support to XRD results. The band gap of CdS crystals were calculated from optical absorption spectra and it’s found to be 2.37eV.

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References


