CHAPTER – 3

SURFACE STUDIES OF CADMIUM SULFIDE (CdS) CRYSTALS
3.1 Introduction

The uniformity and roughness of the surface play an important role in the optical properties of crystals. When the surface is rough, the crystals will be less transparent and the grain boundaries will affect the electrical properties. Since our aim is to use these grown of crystals in Schottky barrier devices, it is necessary to study the device quality of cadmium sulfide (CdS) crystals surface. The surface morphology of the crystals is studied using Optical Microscopy, Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM).

3.2 External Morphology of Crystals (Crystal Habit)

External morphology is a result and reflection of crystal growth. Depending on growth conditions, the same crystal species may show different external forms. Generally, the crystals are never spherical in shape. Although two crystals of a given chemical may appear quite different in size and shape, they always have something in common, known as the Law of Constant Interfacial Angles, proposed by Hauy in 1784. This law states that the angles between corresponding faces of all crystals of a given substance are constant, even though the crystals vary in size and in the development of the various faces (called the crystal habit).

The interfacial angles and lattice dimensions can be measured accurately by X-ray crystallography. Actual crystals of a given substance and a given crystal system can exhibit markedly different appearances when the faces grow at different rates, particularly when these rates vary markedly from stunted growth in one direction, so as to give plates, or by exaggerated growth in another direction, to give needles. [1].

Mostly, all crystals grow approximately equivalent rates in all dimensions. Furthermore, during growth where dislocations and other defects propagate, they do so from the nucleus or seed along specific directions into the bulk of the crystal. In the crystals, which grow as needles or plates, the growth dislocations propagate along the principal growth directions and the crystals remain imperfect (Pamplin 1979). Needle like crystals have very limited applications and plate like crystals need to be favorably oriented. Figure 3.1 show some of crystal habits of hexagonal CdS with approximate growth temperatures [2].

The perfection of the grown crystal is based on,

1. The purity of the starting materials.
2. The quality of the seed crystal.
3. Cooling rate employed and
4. The efficiency of agitation

![Figure 3.1: Some crystal habits of hexagonal CdS [2].](image)

### 3.3 Optical Microscopy

The surface of the crystalline solids may be considered as an abrupt cessation in the periodicity of the lattice network except in the situation where recombination and reordering occur. Close examination of such an ideal surface composed of layers of atoms or ions parallel to this crystal plane, with non-saturated bonds directed to the surface, helps a great deal in understanding the mechanism by which a crystal grow. Therefore, it was worthwhile to make surface characterization of CdS crystals by optical microscopy. The optical microscope, often referred to as the "light microscope", is a type of microscope which uses visible light and a system of lenses...
to magnify images of small samples. Optical microscopes are the oldest and simplest of the microscopes. However, new designs of digital microscopes are now available which use a CCD camera to examine a sample and the image is shown directly on a computer screen without the need for expensive optics such as eyepieces.

In the present work, in order to understand the growth mechanism of crystal of CdS grown by direct vapour transport technique, were examined for their microstructure analysis using a computer aided optical zoom microscope (make: Carl Zeiss, Model: Axiotech 100 reflected light microscope, manufactured by Carl Zeiss Jena, Germany). The operation and function controls of this microscope as well as the overall view of experimental setup are shown in figures 3.2 (a-b).

The sample for microstructural examination is placed on the cover glass slip. The whole set up is mounted on the mechanical stage with the specimen holder (14). Using the Reflected-light illuminance control (11), the lamp voltage is adjusted using the lamp voltage display (10). From the eyepiece (1) and objective lens (17), the surface structure of the sample is viewed. The specimen holder can be moved front-back and left-right using the co-axial stage drive (15) to bring the desired area in the field of view. With the help of a co-axial coarse and a fine drive (13), the specimen holder can be moved up and down and the surface structure can be well focused.

The optical microscope is finally attached to the CCD camera with X–20 magnification. The whole picture of the surface microstructure can be viewed live on the computer screen and stored in its memory. Finally a print out of the well focussed surface microstructure of the specimen is taken. The as grown surfaces of the crystals grown in the laboratory or those which occur in nature offer some features which signify how they have developed under different conditions. Morphology of the as grown surface of the bulk single crystals consist of variety of structure whose study leads to derive the conditions and mechanism of growth.
Figure 3.2: (a) Photograph and (b) Schematic diagram of optical microscope.

Specifications:

1. Eyepiece
2. Binocular Phototube
3. Pushrod (to change beam path)
4. Luminous-field diaphragm slider
5. Compartment for 3D illuminator shutter
6. Pushrod for reflected-light aperture diaphragm
7. Centring screw for reflected-light aperture
8. Reflected-light illumination Equipment
9. Reflected-light filter slider
10. Lamp voltage display
11. Reflected-light illumination Control
12. On/Off switch with pilot lamp
13. Coaxial coarse and Fine drive
14. Mechanical stage with specimen holder
15. Coaxial stage drive
16. Compartment for reflected slider
17. Objective nosepiece
18. Transmitted light illum. equipment
19. Trans. Light luminous – field diaphragm
20. Condenser carrier with Condenser
21. Compartment for DIC slider

In growth from vapour, theory [3] predicts that the growth of a crystal surface with steps will be the result of three processes:
1. Transport of molecule from vapour to surface of solid.
2. Diffusion of adsorbed molecule to steps.
3. Diffusion of molecules along the edge of a step to a kink.

There are two types of surface microtopograph commonly encountered on the as grown flat crystal faces which are not modified by later processes.

a. Well developed crystal faces are in general characterized by the development of step patterns. A surface microtopograph resembling contour (curve) lines of a topographic map or of polygonal morphology is seen on such a face under the reflection microscope. The contours are growth or dissolution steps, which have developed laterally on the faces, caused by spiral growth or two dimensional nucleation growth of dissolution mechanisms and also by the bunching of thinner steps [4-10]. Thus growth hillocks or the pyramids or steps consisting of the pile (mountain) up of steps may be seen. This may occur evenly over the surface or preferentially in the central portion of a face or near the edges. The contour lines may be irregular, circular or polygonal in morphology, smooth or roughed, molecularly thin or very thick in height. They may show spiral patterns, closed loop or be very complicated.

b. Some crystal faces do not exhibit step patterns, but show only striations. Such faces develop in general rather smaller than the above type, but may sometimes develop large enough to be habit controlling size and have low rational indices. In this case the striations are parallel to the edge with the neighbor face of type (a) and consist of a pile up of steps of growth layers developing on the letter face.

### 3.3.1 Impurities and Foreign Particles

It is well known that impurities adsorbed on advancing steps modify the advancing rate drastically. However, the effect of foreign solid particles or misoriented crystallites which have settled on a growing surface can be visually detected both in situ and ex situ observations of step patterns. Since the effect gives a marked influences upon the advance of spiral steps. There are two situations. When such particles are foreign materials or misoriented crystallites of the same compound, a repulsive force is assumed to exist between the edge of the particle and the advancing step front. When the particle is of the same material and has the same orientation with growing surface an attractive force is assumed to exist. In the former
case, the advancing step is retarded around the particle, resulting in the obstacle in a stream. When the advancing step eventually engulfs the particle, there is the possibility that new dislocation will emerge there.

When plural spirals co-exist nearby, they co-operate or interfere with each other and the step pattern is modified accordingly. A variety of step pattern appears, depending upon their mutual separation, their burger vectors and the signs of the neighbouring screw dislocations. How neighbouring spirals cooperate was originally analyzed by Burton et al (1951) and the analysis was applied to observe spirals by Verma (1953) [11-19].

When the Burger vectors of neighbouring screw dislocations are different a continuous or an intermittent fault line appears along the boundary between the territories of the neighbouring spirals. When spiral steps originating from neighbouring screw dislocations separated by larger distance, then two dimensional re-entrant corners appears. Preferential growth lakes place there and the steps advance faster at the re-entrant corners than in other directions. The step patterns are thus modified.

### 3.3.2 Growth Spirals

In the layer-by-layer growth model formulated by Kossel [20] and Stranski [21], the growth rate is limited by two-dimensional nucleation. Growth will not occur unless the energy barrier required for two-dimensional nucleation is overcome, indicating that there should be a critical value of the driving force for growth to take place. In the case of crystal growth from the vapour phase, this value is estimated to be around 25–50% in terms of super-saturation. In real cases, we observe crystals growing under super-saturation as low as 1%. This large discrepancy between the theoretical and experimental values originates from the fact that Kossel [20] and Stranski [21] assumed the crystal to be perfect. Real crystals, however, are imperfect, containing impurities and dislocations. Frank’s spiral growth model has been proposed to account for the growth mechanism of real crystals.

When a screw dislocation outcrops on a smooth interface, a step is created on the surface that has zero height at the dislocation core and a height corresponding to one Burgers vector at the edge of the face. The growth step starting from such a step advances like a spiral staircase around the dislocation, which acts as a prop, as shown in figure 3.3. This is due to the difference in the angular velocity of
advancement of the spiral step at the centre and that at the edge. Since screw dislocation is a self-perpetuating step source, it is not necessary to overcome the energy barrier for two-dimensional nucleation.

Spiral growth is a mechanism that is expected only on smooth interfaces. The assistance provided by screw dislocations is not necessary in the growth of rough interfaces, where an adhesive-type growth operates. The steps of spiral growth layers are one-dimensional interfaces. If the step is rough, the advancing rate is isotropic, forming a circular step pattern. The spiral pattern will be an Archimedean-type spiral. If a step is smooth, the spiral will be polygonal.

![Figure 3.3: Mechanism of spiral growth.](image)

### 3.3.3 Results and Discussions

The micrographs taken for the surfaces of the as grown crystals of CdS in present investigations have been found to possess exceptionally flat faces of which the surface topographic studies were carried out. Study of microstructures suggests a screw dislocation mechanism of the growth CdS crystals as shown in figure 3.4 (a-c) [11, 14, 15]. In general, presence of screw dislocations in grown crystals shows the characteristic property of the growth from gaseous phase. The pattern of growth spirals, both with unique or with multiple Burger vectors strongly depends on the rate of movement of dislocations and atomic steps in different crystallographic directions relative to the faces.
In figure 3.5 (a-c), the multi-layer CdS with flat/smooth surface were observed. On the other hand, the thin platelet with tree like (dendritic) patterns on its face is formed (see figure 3.6 (a-c)) [22, 23]. Furthermore, figure 3.7 (b) shows a hexagonal shape with etched surface. A crack on the grown surface was present on the face as seen in figure 3.7 (c). The different feature of growing crystal and the irregular shape of growth layers might be due to rapid growth (high growth rate) [24].

In all of the figures (3.4 to 3.7), it can be seen that the surfaces are not very clean. This is mainly because of the fact that the photographs of all these crystals were taken prior to giving any surface cleaning treatment (i.e. directly after growth with as grown surfaces). These surfaces can be made smoother by giving some chemical treatment.

Also, the cleaving of samples will reduce such non-uniformities as the inner layer surfaces are expected to have better growth features. In addition to this, air interaction with crystal grown for some time also must take into account.
Figure 3.4 (a-c): A typical spiral growth on the as grown face of CdS crystals.
Figure 3.5 (a-c): A typical smooth surface of the multilayer growth of CdS crystals.
Figure 3.6 (a-c): Cds thin platelet with a nucleation spot act as initiation center of (dendritic) pattern.
Figure 3.7: The optical micrographs of CdS showing that; (a) the presence of growth layers in of CdS crystals; (b) a hexagonal shape with etched surface; (c) a crack visible on the grown surface of CdS crystals.
3.4 Scanning Electron Microscopy (SEM)

To get a clear picture of as grown crystal surfaces, scanning electron microscopy (SEM) of CdS crystal was carried out. The scanning electron microscope is very helpful to study the surface morphology of the materials. The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern.

The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity. The types of signals produced by an SEM include secondary electrons, backscattered electrons (BSE), characteristic X-rays, light (cathodoluminescence), specimen current and transmitted electrons. Secondary electron detectors are common in all SEMs (figure 3.8), but it is rare that a single machine would have detectors for all possible signals.

![Diagram of different signals produced by SEM](image)

**Figure 3.8:** Some types of the different signals produced when high-energy electrons impinge on a material.

The signals result from the interactions of the electron beam with atoms at or near the surface of the sample. In the most common or standard detection mode, secondary electron imaging (SEI), the SEM can produce very high-resolution images of a sample surface, revealing details about less than 1 to 5 nm in size [25 -34]. Due to the very narrow electron beam, SEM micrographs have a large depth of field.
yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. A wide range of magnifications is possible, from about 10 times (equivalent to that of a powerful hand-lens) to more than 500,000 times, (about 250 times the magnification limit of the best light microscopes). Characteristic X-rays are emitted when the electron beam removes an inner shell electron from the sample, causing a high energy electron to fill the shell and release energy. These characteristic X-rays are used to identify the composition and measure the abundance of elements in the sample. Figure 2.9 shows an experimental arrangement of SEM (Model: Phillips, Model: XL 30 ESEM) at Sophisticated Instrumentation Center for Applied Research and Testing (SICART), Vallabh Vidyanagar used in experiment study.

The characteristic X-rays generated are used for the identification and estimation of different elements present in the specimen by energy dispersive spectrometer (EDS) and wavelength dispersive spectrometer (WDS). The depth of focus is much larger than the optical microscope image even at lowest magnifications are one of the major advantages of SEM. The principal of a scanning electron microscope or SEM functions by scanning a finely focused beam of electrons onto a sample. The impinging electrons interact with the samples molecular composition. The energy of the impinging electrons onto a sample is directly in proportion to the type of electron interaction that is generated from the sample. A series of measurable electron energies can be produced which are analyzed by a sophisticated microprocessor that creates a pseudo three-dimensional image or spectrum of the unique elements that exist in the sample analyzed. It is this series of electrons which are deflected by collisions with the samples electrons [35].
3.4.1 Results and Discussions

In present investigations of as grown CdS crystals, for the surface analysis studies (Philips XL 30 ESEM (Shown in photograph 3.9) has been used. SEM images were taken at different magnification for CdS crystal as shown from figure 3.10 to figure 3.14.

Figure 3.10 (a-d) indicates the different magnification of CdS crystals by SEM where confirms the multi-layer growth of crystals as shown in figure 3.10 (b). In figure 3.10 (c) the stepwise growth of hexagonal structures inside the crystal surfaces were observed and the hexagonal CdS crystal which was separately grown with dimensions ~ 317 μm × 382 μm were observed in figure 3.10 (d).
Figure 3.10: Different magnification of CdS crystals by SEM; (a) A hexagonal crystallite of CdS which was incompletely grown with diagonal size ~ 75.2 μm; (b) confirms the multi-layer growth of crystals; (c) the stepwise growth of hexagonal layered structure; (d) The hexagonal crystal of CdS with dimensions ~ 317 μm × 382 μm.

A closer look at the crystallites formed indicated the dimensions of growing crystals varies from 82.8 μm to 548 μm can be seen from the randomly labeled SEM images (figure 3.10 (a-d)). As revealed from figures 3.11 (a-c) some of the crystallites are forming a multi-layer porous structure. Interesting feature in this kind of pores of surface is a good ability of light absorption [36].
**Figure 3.11**: SEM of CdS crystals grown by DVT;(a) and (b) The different magnification illustrated the sheets aggregating with layered structure; (c) Enlarged photographs indicates the surface pores of CdS crystal grown by DVT.

### 3.4.1.1 The Initial Stages of Growth CdS Platelets

There are a number of hypotheses describing platelet growth mechanisms from needles were discussed with more detailed by several authors [2,37-42]. In the present case, higher magnification of CdS crystals has been shown the initial growth of the CdS platelet were the needles (see figure 3.12 (a-d)). Therefore, CdS platelet can be described as a band of coherent c needles. Furthermore, this result of the
initial stage of growing CdS platelet has been supported by transmission electron microscope (refer to chapter 2, figure 2.18 (a-d)).

**Figure 3.12:** SEM of CdS crystals grown by DVT; (a) Many hexagonal pyramids in the initial growth stage, but they became needles after longer growth time; (b-d) Enlarged photographs of needles with length ~5 μm to 60 μm on its surface.

### 3.4.1.2 Types of Defects in CdS Crystal and Factors Affecting on CdS Grown by (DVT)

Practically, the growth of crystals by any kind of techniques has never come without some defect that was due to many reasons could be occur during growth process and non ability to adjustment of various physical imperfections or non ability to observe in situ the growth process of formation, but it can investigate these crystals according to information obtainable from such images.
Generally, the growth of twin can be formed as a result of changes in the stacking during growth. Therefore, temperature fluctuations during growth should be minimized and high temperature gradients during the cool down process avoided. They can be formed in a crystal whether it is growing from vapor, liquid, or solid state.

In the case of a twin boundary, the atomic arrangements on each side of it are mirror images of each other. The grain boundary is considered as a two-dimensional defect, but in reality there is a specific thickness associated with this defect. In general, the grain boundaries contain a high density of interface states that may trap free carriers, cause carrier scattering, and act as sinks for the impurity segregation [43, 44].

Figure 3.13 and figure 3.14 shows that different kind of defects occurs in these crystals. Voids are common type of volume defect that may occur during growth process which is regions where there are a large number of atoms missing from the lattice (refer to chapters 1, section 1.3.3.4). In the present investigation, the three dimensions of the hexagonal pits identified voids defects in crystals grown by DVT showing in figure 3.13 (a-b).

In figure 3.14 (a-c), the twin like flower consists of CdS that grow from a single nucleation centre arranging them in a spherical shape exhibiting flower-like morphologies. Another model of twin is parallel-twin formation in crystal during crystal growth. When a twin boundary is accidentally formed on facet plane, another twin boundary is formed parallel to the first twin after lateral growth is promoted [45] which look like steps structure.

Generally, whatever observed of features neither was twinned nor was any other defect, we suggest that it has a negligible influence on the crystal's properties because these crystals were used for fabrication of Schottky diodes and it give a good response up to high range of temperatures. In addition, the multi-layer growth of the crystallites are dominating growth mechanisms observed [46].
Figure 3.13: SEM of CdS crystals grown by DVT; (a) the three dimensions of pits identified a void defect in crystals grown by DVT; (b) Enlarged photographs of the hexagonal pit defect in crystals grown by DVT.
Figure 3.14: SEM of CdS crystals grown by DVT; (a) and (b) The twin planes like flowers; (c) The parallel-twin formation like steps structure.
3.5 Atomic Force Microscopy (AFM)

AFM is one type of scanning probe microscope, which has an ability to create three dimensional micrograph of a sample surface with a resolution down to the nanometer and angstrom scale. The AFM is one of the foremost tools for imaging, measuring and manipulating matter at the nano-scale. The atomic force microscope (AFM) is not only an excellent tool for recording the surface topography of a sample, but also proven to be a good means for studying the strength of chemical bonds [47-48], the elastic and mechanical properties of macromolecules [49-52] and the intermolecular interactions at the single molecular level [53-55].

AFM is also known as scanning force microscope (SFM) because by using AFM one can image the surface with atomic resolution and at the same time one can also measure the force at nano-scale. This force is between the tip and the sample surface like van der Waal force with resolution in the range of a few nano-newtons. The Atomic Force Microscope (AFM) is being increasingly used in solving processing and materials problems in a wide range of technologies being used in electronics, telecommunications, biological, chemical, automotive, aerospace and energy industries. The materials being investigated include thin and thick film coatings, ceramics, composites, glasses, synthetic and biological membranes, metals, polymers and semiconductors. The AFM is also being applied to the studies of phenomena such as abrasion, adhesion, cleaning, corrosion, etching, friction, lubrication, plating and polishing.

AFM can be used in contact mode like a conventional stylus, in non-contact mode with the probe a few nanometers above the surface (balanced between attractive and repulsive atomic forces) or in intermittent contact mode at the natural frequency of the microlever on which the probe is attached [56]. In short, it operates in three modes viz.

i. Contact Mode AFM [strong (repulsive)-constant force or constant distance]

ii. Tapping mode AFM [strong (repulsive) –vibrating probe]

iii. Non contact mode AFM [weak (attractive) – vibrating probe]

The AFM consists of a microscope force sensor that responds to a force and a detector that measures the sensor response. The sensor is a cantilever with an effective spring constant k. At the end of the lever, is a sharp tip which is used to
sense the force between the tip and the sample. The detector measures the
deflection of the lever. In AFM, we use the laser feedback detection system which
can then be used to determine the force on the tip by using Hook’s law \( F = k z \), where
\( z \) is the cantilever displacement. If the sample is scanned under the tip, the force
between tip and sample surface and image of the sample surface are generated. By
scanning the AFM cantilever over a sample surface and recording the deflection of
the cantilever, the local height of the sample is measured; three dimensional
topographical maps of the surface are then constructed by plotting the local sample
height verses horizontal probe position.

Atomic Force Microscopy (AFM) measures the interaction force between the
tip and the surface. The tip may be dragged across the surface, or may vibrate as it
moves. The interaction force will depend on the nature of the sample, the probe tip
and the distance between them. AFM provides a 3D profile of the surface on a
nano-scale, by measuring the forces between a sharp probe (<10 nm) and surface at
very short distance (0.2-10 nm probe-sample separation). The probe is supported on
a flexible cantilever. The AFM tip “gently” touches the surface and records the small
force between the probe and the surface. The motion of the probe across the surface
is controlled similarly to the STM using feedback loop and piezoelectronic scanners
(figure 3.15 (A, B) and the Photographic view of Atomic Force (AFM) are shown in
figure3.16.

The primary difference in instrumentation design is how the forces between
the probe and sample surface are monitored. The deflection of the probe is typically
measured by a “beam bounce” method. The beam-bounce method is now widely
used as a result of the excellent work by Alexander and colleagues [57]. In this
system an optical beam is reflected from the mirrored surface on the back side of the
cantilever onto a position-sensitive photodetector. In this arrangement a small
deflection of the cantilever will tilt the reflected beam and change the position of the
beam on the photodetector. A third optical system introduced by Sarid [58] uses the
cantilever as one of the mirrors in the cavity of a diode laser. The motion of the
cantilever has a strong effect on the laser output, and this is exploited as a motion
detector. A semiconductor laser diode is bounced off the back of the cantilever onto
a position sensitive photodiode detector.
Figure 3.15 (A, B): Schematic of AFM instrument showing “beam bounce” method of detection using a laser and position sensitive photodiode detector.

Figure 3.16: Scanning probe microscope (AFM).

❖ **Specifications:**
- Available Modes (Contact & Non-Contact AFM, STM, LFM, EFM, MFM, Nanolithography and Nano-manipulation)
- 100 μm Scanner- Z-range: 7.5 μm
- DAC XY-Resolution: 0.25 Å & Z- Resolution: 0.025Å
- μm Scanner- Z-range: 2.5 μm;
- DAC XY-Resolution: 0.0013 Å & Z- Resolution: 0.009 Å with associated image analysis software.
This detector measures the bending of cantilever during the tip is scanned over the sample. The measured cantilever deflections are used to generate a map of the surface topography.

### 3.5.1 Primary Modes of Imaging

The primary modes of imaging (1) contact mode (2) Intermittent mode and (3) non-contact mode are described below:

**Figure 3.17:** Force Vs distance (tip to sample) curve.

#### 3.5.1.1 Contact Mode AFM (Repulsive VdW)

When the spring constant of cantilever is less than surface, cantilever bends. The force on the tip is repulsive. By maintaining a constant cantilever deflection (using the feedback loops) the force between the probe and the sample remains constant and an image of the surface is obtained.

**Advantages:** fast scanning, good for rough samples, used in friction analysis.

**Disadvantages:** at a time forces can damage/deform soft samples (however imaging in liquids often resolves this issue).

#### 3.5.1.2 Intermittent Mode (Tapping)

The imaging is similar to contact. However, in this mode the cantilever is oscillated at its resonant frequency. The probe lightly “taps” on the sample surface
during scanning, contacting the surface at the bottom of its swing. By maintaining constant oscillation amplitude a constant tip-sample interaction is maintained and an image of the surface is obtained.

**Advantages:** allows high resolution of samples that are easily damaged and/or loosely held to a surface; good for biological samples.

**Disadvantages:** more challenging to image in liquids, slower scan speeds needed.

### 3.5.1.3 Non-Contact Mode (Attractive VdW)

The probe does not contact the sample surface, but oscillates above the adsorbed fluid layer on the surface during scanning (all samples unless in a controlled UHV or environmental chamber have some liquid adsorbed on the surface). Using a feedback loop to monitor changes in the amplitude due to attractive VdW forces the surface topography can be measured.

**Advantages:** Very low force exerted on the sample (10-12 N), extended probe lifetime.

**Disadvantages:** generally lower resolution; contaminant layer on the surface can interfere with oscillation; usually need ultra-high vacuum (UHV) to have better imaging.

### 3.5.2 Surface Roughness Parameters and Statistical Measures with AFM

The surface roughness can be quantified using a variety of different parameters [59] that can be divided into two groups. (1) Single values to describe the roughness and (2) statistical measures of the roughness. Two common single value parameters for roughness are the arithmetic roughness (Ra) and the rms roughness (Rrms). Unfortunately, these two parameters only describe the vertical roughness of a surface.

Two surfaces with identical vertical roughness can have a very different surface morphology [60, 61], and a measure of the horizontal roughness is needed to accurately specify their roughness distinctly [62]. Statistical measures of surface roughness provide a more complete description of the surface than single valued parameters [60]. Two commonly used statistical measures of surface roughness are the bearing ratio and the power spectral density (PSD).

The bearing ratio is a useful parameter for characterizing abrasive wear of the surfaces and the PSD is the power spectrum of the Fourier transform of the surface.
profile [60] which provides useful information on the geometric structure of the surface. In particular, it is useful for detecting periodic structure in the profile. The meanings of all such parameters are discussed below.

### 3.5.2.1 Roughness Average /Arithmetic Roughness $R_a$

In general, the roughness average can be considered as the arithmetic mean deviation of all the points or it can be defined as the average deviation of roughness of all points in the profile from a mean line over the evaluation length [63]. The arithmetic roughness $R_a$ of a surface can be expressed as

$$R_a = \frac{1}{N} \sum_{j=1}^{N} |r_j|$$  \tag{3.1}

Where $N$ is the number of data points of the profile and

$$r_j = z_j - \bar{z}$$

Where $z_j$ are the data points that describe the relative vertical height $z_j$ of the surface and $\bar{z}$ is the mean height of the surface given by the equation

$$\bar{z} = \frac{1}{N} \sum_{j=1}^{N} z_j$$ \tag{3.2}

### 3.5.2.2 Root Mean Square Roughness $R_q$

Root mean square roughness is defined as “The average of the measured height deviations taken within the evaluation length and length measured from the mean line”[63]. It can be mathematically expressed as

$$R_q = \sqrt{\frac{1}{N} \sum_{j=1}^{N} r_j^2}$$ \tag{3.3}

### 3.5.2.3 Maximum Profile Peak Height $R_p$

It is defined as “the height of the maximum/highest high intensity peaks in the roughness profile over the evaluation length” [64]. The maximum profile peak height is represented mathematically as

$$R_p = \left| \max_{1 \leq j \leq N} r_j \right|$$ \tag{3.4}

### 3.5.2.4 Maximum Profile Valley Depth $R_v$ or $R_m$

It is defined as “the depth of the deepest valley in the roughness profile over the evaluation length” [64] which may be given mathematically as
3.5.2.5 Maximum Height of the Profile $R_t$ or $R_{p-v}$

Maximum height of the profile basically is a measure of the maximum peak to valley height in the roughness profile. The exact definition of it may be given as “The absolute value between the highest and lowest peaks”[65]. The mathematical expression used to calculate the parameter is

$$R_t = \left| \min_{1 \leq j \leq N} r_j \right| + \left| \max_{1 \leq j \leq N} r_j \right|$$

3.5.2.6 The Amplitude Distribution Function (ADF)

The amplitude distribution function is a probability function that gives the probability that a profile of the surface has a certain height $z$ at any position $x$ [66].

3.5.2.7 The Bearing Ratio Curve (BRC)

The Bearing Ratio Curve is related to the ADF. It is the corresponding cumulative probability distribution. The bearing ratio curve is always integral (from the top down) of the ADF [66]. The bearing ratio ($t_b$) is defined as the length of the profile above a horizontal line through the distribution [67] and is typically shown as a graph in which the ordinate is the height below the highest peak in the profile. This makes the bearing ratio curve more accurate reflection of the vertical roughness of the surface than arithmetic or RMS roughness. The length of the surface is a measure of the vertical roughness of the surface (of the crystal) whereas the shape of the bearing ratio curve is an indication of the topography of the surface [68]. It finds much greater use in evaluating surface finish.

3.5.2.8 Power Spectrum

The most important property of rough surfaces is the surface roughness power spectrum. It determines the contact area between two solids and can provide both lateral and longitudinal information. Thus, it is more informative measurement than all the statistical quantities.

Surface roughness is often understood as a departure of the roughness parameters from the planarity. A convenient way of describing surface roughness is to represent it in terms of profile height $z (x, y)$. For typical digitized AFM scans, the values of $x$ and $y$ are quantized. To determine PSD, one needs to transform 2D AFM
images from real space to reciprocal space. Two types of Transformations are used by various authors: one is the Fast Hartley transform (FHT) [69] and the other is the Fast Fourier transform (FFT) [70-76]. Even though the 2D FFT and FHT give us a transformed version of the reciprocal space, it is still difficult to make use of this 2D information. The standard method to solve this problem is to extract a 1D magnitude of the 2D transform; that is, a 1D power spectral density is plotted against the spatial frequency. For a typical 2D AFM Scan, it consists of 250 000 (i.e. 512 × 512) data points, but the 1D PSD requires 512 pieces of information to describe the surface roughness. This method was proposed independently by Dumas et al. [68] and Strausser et al. [69,74]. In AFM, one and two-dimensional power spectral density (PSD) is used to characterize the structure of the surfaces. In the present work, (1D) PSD is considered, as the simulations used are line scans, not two dimensional images. The (1D) PSD is given by the relation [74],

\[ PSD_{1D} = \frac{1}{L} \left( \frac{\pi}{2} \int y(x)e^{i(px)}dx \right)^2 \]

Where \( L \) is the length of the profile and \( y(x) \) is the profile.

The power spectral density is advantageous because it allows comparison of the roughness data taken over various spatial frequency regions. Such methodology also offers a convenient representation of the direct space periodicity and amplitude of the roughness.

### 3.5.3 Results and Discussions

The as-grown crystals of CdS were viewed under the non-contact AFM mode. Silicon nitride tip was used to obtain topographic images of the surfaces of the crystals. One can also obtain various Line analyses spectrums from real images by the Digital Instruments 2SPM controller using di CP-II ProScan 1.9 software. Figure 3.18 (A, B) and figure 3.19 (A, B) shows the 2D and 3D AFM images covering an area of 2μm × 2μm for CdS crystal samples 1 and 2 respectively. The images are computer generated and the original data can be manipulated so that the surface of interest can be viewed from different directions. Distance scales in the x, y and z directions are marked on the 3D images and the z scale can be exaggerated as required.

The 3D images (maximum 256 × 256 points) do facilitate over all visualization of the crystals surface. An image in a 3D format gives a rendition of
what the surface topography actually looks like. That is, the data is displayed in the x, y and z axis. Often the scale between the x, y and z axis are not equal. The surface features are very small with relationship to the x and y dimensions; however, in 3D image they look large. This figure reflects that the CdS crystal possess flat surface with some hilly (also valley) regions. The two dimensional image shows the x and y axis and color is used to depict the height of image. An AFM image displayed in the 2D format looks much like an image obtained from a traditional microscope such as an optical microscope.

To know the surface morphology of two samples for CdS crystals, the line analysis is carried out in detail. The line profile is a two dimensional profile or cross section extracted from an AFM image. This may be taken horizontally, vertically or at obtuse angles. The result of lines analysis for the two samples surface profile along the chosen traverse length can be printed out together with the height profile, histogram, power spectrum, bearing ratio along with various statistical parameters is listed in table 3.1 and table 3.2 for CdS crystal samples 1 and 2 respectively.

AFM analysis shows the presence of uniform with crack surface morphologies as in figure 3.18 of the as- grown CdS crystal. The line – 1, line – 2, line – 3, line – 4 and line - 5 (shown in figure 3.18 (A)) had drawn on the surface of the CdS crystal show indirectly the typical arrangement of the growth features in those regions. The height profiles taken along the horizontal line – 1 to line - 5 of the AFM image of CdS crystal, it can be seen that a maximum roughness was corresponding to line-1 and minimum roughness (smooth/uniform) was corresponding to line-5 [75, 76] as shown in table 3.1.

This reveals the fact that the difference between the peak p and the valley z or v values (R_{p,v}) are around 55.19 nm (maximum) and 18.44 nm (minimum) of line – 1 and line – 5 respectively, indicating crystal at location of line 1 has a maximum peak to valley difference than at location of line – 5.

The height distributions (Histograms) obtained from the 2D AFM image. The histogram is a continuous bar diagram in which each column represents a height range. The height of each column represents the number of image pixels which have a height value in a particular range. The histograms of line-5 shown in figure 3.18(C), indicates that the height distribution is asymmetric [77]. It is negatively skewed, because the mean value is smaller than the median value.
The asymmetry, whether positive or negative, expresses a little bit of non-uniformity in that particular region within the image. The rms (R_q) and average (R_a) roughness values (maximum) for line 1 are found to be 14.42 nm and 10.51 nm, whereas for line 5 these values (minimum) are 3.267 nm and 2.212 nm respectively, indicating that there is significant difference in average and rms values of peaks across these lines while four lines 2, 3 and 4, compared with lines 1 and 5. It may be noted that these parameters indicate roughness in vertical direction. However, these two single value parameters (i.e. R_{rms} and R_{a}), though simple and reliable, make no distinction between peaks and valleys and do not account for the lateral distribution of surface features. The mean height indicates the central value in the roughness profile over the evaluation length and is found to be 25.87 nm, while median height is a midpoint on the roughness profile over the evaluation length such that almost of the data fall above it which turns out to be 26.55 nm.

The horizontal measurement of roughness can be studied from the height profile (figure 3.18 (D)), which indicates the number of intersections that the profile makes with the mean line of the profile over a specified distance. The bearing ratio is expressed in percentage which is the ratio of the length of the bearing surface at any specified depth in the evaluation area.

A more complete description is provided by the power spectral density (PSD) calculations of the surface topography, which perform a decomposition of the surface profile into its related spatial wavelengths and allows comparison of the roughness measurements over different spatial frequency ranges [78]. Thus, the variation of height fluctuations can be represented more accurately through the power spectral density (PSD). This quantity can be calculated by performing a fourier transform of the 2D height date [79, 80]. The power spectral density curves corresponding to line 5 is shown in figure 3.18 (E). The curve indicates that the overall surface of CdS crystal is homogeneous. However, a number of peaks consists more at lower frequency, corresponding to the large features in the image. At higher spatial frequencies the amplitude of the PSD curves gradually decreases. This PSD curve also provides information across the entire frequency range of the scanned surface (2μm × 2μm) including waviness (mid frequency) and form (lower frequency). The peaks in the PSD indicate the periodicity of the surface. The peaks in the PSD indicate the periodicity of the surface. The frequency of each peak gives the length that defines
this periodic surface and the spread in the peak indicates the magnitude of the deviation from the average value.

**Figure 3.18:** AFM images of the as-grown CdS crystal (*sample 1*): (A) 2D and (B) 3D (C) histogram (D) height profile and (E) power spectrum.

In the same way, the second sample shown in figure 3.19 has been analyzed. By comparing the data obtained of the two samples for CdS crystals, it is clearly observed that the overall surfaces of both samples are almost flat surface with some irregularity. Additionally, the sample 2 present in figure 3.19 has a lower roughness, surface than the sample 1 presented in figure 3.18 according to the data extracted from AFM for both samples which listed in table 3.1 and table 3.2.
Figure 3.19: AFM images of the as-grown CdS crystal (sample 2): (A) 2D and (B) 3D (C) histogram (D) height profile and (E) power spectrum.
Table 3.1: Line analyses of the AFM profiles of the as-grown CdS crystal (sample 1).

<table>
<thead>
<tr>
<th>Line</th>
<th>$R_{p-v}$ (nm)</th>
<th>Rms Rough $R_d$ (nm)</th>
<th>Ave. Rough $R_q$ (nm)</th>
<th>Mean $H_t$ (nm)</th>
<th>Median $H_t$ (nm)</th>
<th>Arc Length (um)</th>
<th>Bearing Ratio @ 30.0%</th>
<th>Bearing Ratio @ 80.0%</th>
<th>Peak $R_p$ (nm)</th>
<th>Valley $R_v$ (nm)</th>
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Table 3.2: Line analyses of the AFM profiles of the as grown CdS crystal (sample 2).

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<th>$R_{p-v}$ (nm)</th>
<th>Rms Rough $R_d$ (nm)</th>
<th>Ave. Rough $R_q$ (nm)</th>
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<th>Arc Length (um)</th>
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Summary

The surface of CdS crystals investigated using the Optical Microscopy, Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). Optical Microscopy suggests a screw dislocation mechanism of the growth CdS crystals and the thin platelet with tree like (dendritic) patterns on its face due to rapid growth. The multi-layer porous structure and twiny defect were observed by Scanning Electron Microscopy. The investigation of the initial growth stage was coming to be supportive of TEM results which were needles. The commons observed by Optical Microscopy and Scanning Electron Microscopy were the multi-layer structure to be dominated structure. In addition, the commons observed by Optical Microscopy and Scanning Electron Microscopy and Atomic Force Microscopy were a flat Surface with some irregularity visible on the grown crystals.
References


