Synthesis of single crystalline CdS nanocombs and their application in photo-sensitive field emission switches

3.1 Introduction:

This chapter describes the systematic study of the influence of the process variables such as position of the substrates in horizontal tube furnace, effect of local temperature, flow rate of the Ar gas, catalyst thickness, and amount of precursor on the structural and morphological features of CdS films. The synthesized nanostructures were characterized by various techniques. Finally a possible mechanism, describing the evolution of different morphologies, growth parameters along with various interlinked factors responsible for the variety of the CdS nanoforms, are discussed in detailed.

Before beginning with the synthesis and field emission work of the CdS nanoforms, some interesting studies on the field emission and photo-enhanced field emission of aligned CdS nanowires were performed by the author [1]. These results have proved to be a key factor behind this work. Aligned CdS nanowires used for the field emission study were synthesized by solvothermal route on Cd foil.

3.2 Experimental detail-aligned CdS nanowires:

Aligned CdS nanowires have been fabricated by solvothermal route. Around 0.01 mol of Cd granules (Loba Chemie. 99% assay) were weighed and were beaten to foils (~ 1 mm thickness). Thiourea (double the moles of Cd foil) was used as the source of sulfur.

# this work was carried out at IACS, kokatta by datta et al. [1] and is not being claimed as part of the work presented in this thesis.
Both were taken in a Teflon-lined stainless steel autoclave and filled with ethylenediamine up to 80% of the total volume (100 ml). The autoclave was maintained at different temperatures (150-250 °C) for variable time period (5-48 h). The suitable specimen with aligned CdS nanowires was used for field emission study.

Detail of the optimization parameters for aligned growth of the CdS nanowires have been published by Datta et al. [1]. Few of the characterizations of the aligned CdS nanowires are summarized briefly.

3.3. Characterization:

3.3.1 SEM Studies:

Figure 3.1 shows Scanning Electron Microscope (SEM) image of highly dense aligned CdS nanowires synthesized at optimized conditions (temp ~ 250 °C and reaction time ~ 7 h).

Figure 3.1 shows SEM image of the as-synthesized aligned CdS nanowires.
3.3.2 TEM and HRTEM studies:

Transmission Electron Microscope (TEM) and High Resolution TEM (HRTEM) images of aligned CdS nanowires prepared at 250 °C for 7 hrs shown in Figure 3.2a, b indicates that the as-synthesized nanowires have a smooth faceted and single crystalline nature with a length and diameter of ~ 8 μm and ~ 50 nm. The HRTEM image of one of the nanowires depicts distinct lattice fringe spacing. Single crystalline nature of the nanowires is also confirmed by the selected area electron diffraction (SAED) shown as inset of Figure 3.2b which indicates that the nanowires are of single crystalline nature.
Figure 3.2 (a) TEM image of the CdS nanowires produced after 7 h of deposition at 250 °C and (b) corresponding HRTEM and SAED (inset) pattern.

3.4 Field emission study-aligned CdS nanowires:

The field emission current density-applied field (J-E), characteristic of the aligned CdS nanowires is depicted in Figure 3.3a. The best oriented specimen was chosen for the field emission measurement, expected to show an enhancement in the field emission properties [2]. The turn-on field, defined as the field required to draw an emission current density of ~0.1 μA/cm², was found to be ~ 0.68 V/μm. As the applied voltage was increased further, the emission current increased very rapidly and an emission current density of ~31 μA/cm² was drawn at an applied field of ~1.16 V/μm.

The observed value of turn-on field is better than values reported for quasi aligned and aligned CdS nanowires [3] and nanotubes [4]. The observed value of turn-on field is also lower than those reported for various ZnO nanostructures such as nanowires [5], nanorods [6], and other semiconducting nanostructures such as copper oxide nanowires [7].
The lowest value of observed turn-on field is attributed to the nanometric dimension and high aspect ratio of the aligned CdS nanowires. The Fowler-Nordheim (F-N) plot, that is, ln(J/E^2) versus (1/E), derived from the observed J-E characteristic, is depicted in Figure 3.3b. The F-N plot shows an overall linear behavior with a decrease in the slope (saturation tendency) in the very high applied field range. Such type of F-N plot exhibiting a tendency towards saturation, at a very high applied field is consistent with previous published results [3, 8].
The field emission-time (I-t) plot recorded at a base pressure of $1 \times 10^{-8}$ mbar is shown in Figure 3.4. The emission current stability of the aligned CdS nanowire emitter has been investigated at the preset current value of 5 µA (at applied voltage of $\sim 1$ V/µm) over the duration of 4 hr. The emission current is seen to be stable over the duration of the measurement characterized by fluctuations in the form of “spikes”. The appearance of the “spikes” in the emission current is due to the adsorption, desorption, and migration of the residual gas molecules on the emitter surface. The striking feature of the field emission behaviour of the aligned CdS nanowire emitter is that the average emission current remains nearly constant over the entire duration and shows no signs of degradation. This is a very important feature, particularly for the practical application of the emitter material as an electron source. A post field emission SEM study indicates no significant change in the overall surface morphology of CdS nanowires emphasizing that CdS nanowires are mechanically robust against the ion bombardment and stresses induced due to the intense applied electric field.

A typical field emission image, captured at the applied field of $\sim 1.1$ V/µm, is shown in the inset of Figure 3.4.

![I-t plot of the CdS planar emitter with inset showing the image recorded during emission.](image-url)
The image shows a number of tiny spots, which correspond to emission from the most protruding CdS nanowires. The temporal changes in the intensity of the spots are observed to be commensurate with the emission current fluctuation as seen in the I-t plot. In the present case, the current density J is estimated by considering the entire area \((0.36 \, \text{cm}^2)\) of the emitter.

CdS is known to be a good photoconducting semiconductor [9]. In order to exploit its photoconductivity, we performed a photo-assisted field emission study by exposing the cathode to a constant intensity of incident light. For these investigations, the cathode was illuminated from the "front side" by keeping halogen lamp \((1300 \, \text{W/m}^2)\) at a distance of 10 cm from the view port of the chamber. The intensity of incident light at the cathode site was measured using a photocell. A plot of photo-assisted field emission current versus time is shown in Figure 3.5.

![Figure 3.5 A plot of photo-assisted field emission current versus time indicating the photo-switching property of the aligned CdS nanowires.](image)

It is seen that the emission current level increases suddenly in the presence of light, and it rapidly decreases to the original set value as the lamp is switched off. The rise in the current level was seen to be \(~50\%\) of the initial value, and the light-induced
effect on field emission current was observed to be reproducible. The enhancement in the emission current upon illumination is attributable to the photoconductivity of CdS. Sharma et al. have investigated the light-induced effect on field emission characteristics of CdTe sub-micrometer structures [10].

It is well known that field emission is a function of the morphology of the emitter. The field emission studies of CdS having different nanoforms are, therefore, carried out.

3.5 Experimental detail-CdS nanoforms:

3.5.1 Optimization of the synthesis parameters (for controlled synthesis):

3.5.1.1 Influence of the position of substrates:

As discussed in the chapter II, thermal evaporation technique is quite sensitive technique which strongly depends upon the various parameters such as position of the substrates with respect to the position of the source, gas flow and temperature of the source etc. Our primary aim was to optimize the system parameters for the controlled and reproducible growth of nanostructures. For the purpose of optimization, several experiments were carried out. Position of the substrate i.e. local temperature of the substrate is found to be a key factor, responsible for the growth of various nanoforms. The temperature affects growth in three ways:

1) size of the catalyst droplets
2) the condensation of vapors and
3) the length of surface diffusion of adsorbed vapor species [11].
Figure 3.6 shows the plot of the local temperature (for the source temperature of ~ 800 °C) versus distance from the centre of the horizontal zone furnace. As shown in the Figure, it is clear that the temperature systematically decreases from the center to the end of the furnace.

![Graph showing temperature decrease](image)

Figure 3.6 Dependence of local temperature at different position of substrate from the center of the horizontal zone furnace.

At the source (CdS powder) temperature of ~ 1000 °C, the temperature of the specimen which is placed at the distance of 28 cm away from source is found to be ~ 865 °C. The growth species at this position are energetic enough to remain in the form of vapor and hence do not get condensed, so there is a high rate of desorption and re-evaporation which leads to short, thin, sparse wires as shown in Figure 3.7a.

The effects of surface diffusion and the condensation of vapor create strong differences in the growth rate in different temperature zones. As the temperature decreases the ideal condition occurs for formation of comb-like morphology with a diameter of the spikes ~ 200 nm with high number density at the temperature ~ 850 °C. As the temperature continues to decrease (~ 840 °C), the nanobelts with length ~ 50 μm, width ~ 1.5 μm and small thickness ~ 80 nm are observed. High temperature and constant high flux of vapors favors the growth of nanocombs and nanobelts as shown...
in Figure 3.7b,c. At a temperature (~ 820 °C), lower than that required for the formation of nanocombs and nanobelts, uniform growth of the nanowires with length ~ 50 μm and diameter of ~ 150 nm are seen with Au particles at their apex. In this case temperature is good enough to build up the nanodroplets of Au which further react with vapors having moderate concentration which results in the uniform growth of the nanowires as shown in Figure 3.7d. At the lower temperature, due to the variation of local concentration of depositing vapors, non uniform spikes with difference in the size distribution is clearly seen (Figure 3.7e). At the temperatures below ~ 820 °C the nanowire growth ceases as seen in Figure 3.7f, g, h.

At the lowest end of the deposition range, where the substrate temperature is low enough, the vapor has little energy and the molecular species hence get deposited exactly where they land, creating a rough and uneven film. The intermediate temperature zone has enough vapors to grow wires and in there is enough energy to allow the species to diffuse and move to the energetically favorable plane but not high enough to cause significant re-evaporation. This zone produces the nanocombs and nanobelts. Nevertheless, the rate of flow of gas also plays a vital role in the formation of typical morphology.
Figure 3.7 SEM images of the CdS nanoforms (a) micron sized sheets (b) nanocombs, (c) nanobelts (d) nanowires, (e) sub-micron sized spikes with non-uniform diameter, (f) micron sized rods (g) densely grown particles, and (h) nanoparticles, found at different position of the substrates with respect to the position of source (from centre).
3.5.1.2 Influence of the catalyst (Au) thickness:

Figure 3.8 SEM images of the CdS nanowires with different Au thickness. Average diameter of 150 (a, b), 250 (c, d), and 350 nm (e, f) found for the Au thickness of ~ 3, 6, and 9 nm.

Figure 3.8a-f shows the SEM images of CdS nanowires grown at constant parameters such as Ar gas flow and substrate temperature with different catalyst film thickness. It is seen that the diameter of the CdS wire increases with the thickness of
film. Figure 3.8a,b shows the diameter of ~ 150 nm for the Au thickness of ~ 3 nm, while for the ~ 6 nm thickness it is ~ 250 nm (Figure 3.8c,d). As the thickness is increases further (~ 9 nm), the average diameter is found to ~ 350 nm (Figure 3.8e, f).

Due to minimization of free energy [12], the diameter of the wires is related to the size of the catalytic droplets. When thinner catalytic films are used dense areas of wires can be seen (Figure 3.8a). The formation of a smaller catalytic island implies the formation of denser island areas.

As the field emission is sensitive to the relative dimensions of the emitter, Au catalyst with the film thickness of ~ 3 nm on Si (111) substrates is used for all the synthesis experiments.

3.5.1.3 Influence of gas flow rate:

A variation in the Ar flow rate directly influences the shape and size of nanoforms i.e. diameter of nuclei. This is important because it can change the relative Cd and S concentration inside the tube. The variation in the Cd and S partial pressures directly affects the process of condensation and, therefore, characterizes the growth. In these experiments, we used Ar with a constant concentration varying from 150 standard cubic centimeters per minute (sccm) to 350 sccm. Figure 3.9 shows SEM micrographs of specimens grown at the same temperature (source temperature: 1000 °C, substrate position: 31 cm) with the gas flow varying from 150 sccm to 350 sccm. It is observed that at lower flow rates (150 sccm) there are smaller and thicker rods (chunks) which are larger in diameters as shown in the Figure 3.9a. When the flow rate is increased to 250 sccm the relative Cd:S ratio seems to boost the growth and create longer wires as observed in Figure 3.9b. For higher flow rates (350 sccm) the growth species is seen to be quite dense with non uniform chunks. This leads to a higher supersaturation, leading to extraneous nucleation with different morphologies of growth as shown in Figure 3.9c.
Figure 3.9 SEM images showing the dependence of morphology on the Ar flow rate which seems to be a more crucial parameter for growth of nanoforms.

In this study it is seen that for the growth of well defined nanostructure, along with uniformity on the whole area of the substrate, moderate and constant Ar flow is required.
3.5.1.4 Influence of the amount of precursor:

Figure 3.10 Effect of excess amount of precursor on the corresponding dimensions of nanostructures.

The study shows that the appropriate amount of precursor is also an important parameter which plays a crucial role in controlling the dimensions of corresponding nanostructures. As discussed in the previous section, regarding the dependence of relative dimensions of the nanoforms on local condensation, saturation and concentration of the evaporating vapors, the quantity of the precursor taken for the
synthesis of the controlled nanostructures plays a significant role. In the present investigation the amount of the precursor varies from 10 mg to 1 g. Keeping other parameters constant, several experiments were carried out with different amount of precursor. Morphologies such as nanocombs, nanobelts and nanowires were found with lower quantity of precursor (10 mg). As the quantity of the precursor is increased the relative dimensions of the nanoforms increases significantly. With excessive intake of Cd and S vapors species the growth of the nanoforms changes: for example, such as nanocombs (Figure 3.10a, b) with diameter ~ 1 μm are found to grow. Nanobelts become nanoribbons with width ~ 30 μm and length ~ 500 μm and thickness ~ micrometer (Figure 3.10c, d) and the ultra long nanowires with length ~ 750 μm (Figure 3.10e, f) are noticed. The inset of Figure 3.10f is the optical image of the ultra long nanowires grown on Si substrate.

3.5.1.5 Other parameters:

Ramp of temperature, i.e. rate at which the temperature of the source increases is also an important parameter. The rate of condensation of the vapors depends upon how slow or how fast they are created. In our case ramp of 20 °C/min is seen to be optimized factor for the growth of the well shaped nanoforms. At higher rate, mix morphologies such as nanobelts and nanowires are seen at a position ~ 31 cm away from the source material with nanobelts being dominant form.

Deposition time (duration) is also varied during the experimentation. It is seen that for the same quantity of the precursor there is no effect of the duration of the deposition on the morphology of the CdS nanoforms. For a small duration of reaction, a quantity of precursor is seen to be partially evaporating but due to the normal cooling of the furnace, the remaining precursor also gets evaporated during cooling.

For the investigation of the detailed structural, optical, field emission and photosensitive field emission studies only three morphologies such as nanocombs,
nanobelts and nanowires are taken into considerations which are repetitively observed at a distance of ~ 29, ~ 30 and ~ 31 cm away from the source and they are found to possess regular and specific shape and size.

3.5.2 Synthesis parameters-CdS nanocombs:

This chapter describes the systematic investigations on the synthesis, structural, optical, field emission and photo-sensitive field emission properties of CdS nanocombs.

The method for the synthesis of single crystalline CdS nanocombs is based on thermal evaporation of high-purity CdS powder (99.99%, Alfa Aesar) under controlled conditions, using Au as a catalyst. An alumina boat, filled with appropriate amount of CdS powder was placed in the middle of the quartz tube of programmable temperature controlled furnace. The gold coated silicon substrate (1 cm x 1 cm) was kept at a distance of 29 cm downstream the gas flow from the center. The CdS nanocomb morphology is observed repetitively only at this position of substrate. The Si substrate was first ultrasonically cleaned in acetone for 20 min and then sputter-coated with a thin (~ 30 Å) layer of Au film. Initially the reaction chamber was flushed with Ar with flow rate of 100 sccm for an hour followed by heating up to 1000 °C with the ramp of 20 °C min⁻¹ and was kept at this temperature for 40 min with constant Ar flow of 250 sccm. After the furnace was cooled to room temperature, the Ar gas flow was turned off. A yellow wool-like product was found on the entire surface of the gold coated Si substrate. This as-synthesized product was used for further characterization.
3.6 Results and discussion-CdS nanocombs:

3.6.1 SEM studies:

Figure 3.11 depicts the typical SEM images of CdS nanocombs. Figure 3.11a indicates wide coverage of CdS nanocombs on the entire Si substrate. A magnified SEM image (Figure 3.11b,c,d) clearly indicates the formation of nancomb like structures with asymmetric growth of spikes under experimental conditions. These spikes have a diameter ~ 200 nm and length ~ 3 μm.

![SEM images of CdS nanocombs](image)

Figure 3.11 SEM images of as-synthesized CdS nanocombs grown on Si substrate (a) lower magnification image of the CdS nanocombs and (b), (c) and (d) close up view of the CdS nanocombs.
After scanning the entire surface of the specimen, it was clear that the growth of the CdS nanocombs was highly asymmetric. The composition of the CdS nanocombs was analyzed by Energy Dispersive X-ray Spectrometer (EDS), and the pattern is shown in Figure 3.12. Elemental analysis shows that the atomic ratio (Cd:S) is ~ 1:1, (52.7:47.3 at %) which is consistent with the stoichiometric CdS within the experimental error.

![Figure 3.12 EDS spectrum of the CdS nanocombs.](image)

3.6.2 X-ray diffraction studies:

The crystalline phase of the product with its crystallographic orientation was identified by X-ray diffraction studies. Figure 3.13 depicts the XRD of the CdS nanocombs synthesized by simple thermal evaporation technique. All the reflection peaks can be indexed to the wurtzite CdS phase with lattice constants $a = 4.14 \text{ Å}$ and $c = 6.72 \text{ Å}$, consistent with the reported values (JCPDS Card No. 41-1049), indicating that the CdS nanostructures crystallize in the pure wurtzite form belonging to the space...
group P63mc and show no evidence of a mixed phase of cubic symmetry. No diffraction peaks due to impurities and other phases, such as CdO, Cd, S, were detected, indicating the high purity of the product.

Figure 3.13 X-ray diffraction pattern of CdS nanocombs.

3.6.3 Photoluminescence (PL) study:

Photoluminescence (PL) spectroscopy is an effective method to evaluate the nature of transitions and defects in materials. Usually, two emission bands are observed for CdS nanostructures: excitonic and trapped state luminescence, respectively [13].
Figure 3.14 Photoluminescence recorded at room temperature.

The absence of the emissions from the surface and deep states associated with the defects and impurities demonstrate that these single-crystal CdS nanocombs possess high quality optical properties and should be excellent building blocks for photonic devices. The room temperature PL of the as-synthesized CdS nanocombs film measured in the spectral range of 470-750 nm is shown in Figure 3.14. A prominent green emission band at ~ 520 nm was noticed which is the characteristic emission of the bulk CdS. A similar peak was also reported by Kar et al. [14].
3.6.4 TEM and HRTEM study:

The morphology and the crystalline nature of as-synthesized product were further confirmed from the transmission electron microscopy (TEM). Figure 3.15a shows TEM image of a single CdS nanocomb (inset also) indicating uniform length, smooth facets. The corresponding selected area electron diffraction (SAED) pattern is as shown the inset.
Figure 3.15 (a) TEM image of the CdS nanocomb and insets are the TEM and SAED of the CdS nanocomb and (b) HRTEM image of individual nanocomb with FFTED pattern as inset.

For the TEM observation a sub micron size CdS comb was chosen. A representative high resolution TEM (HRTEM) image of the CdS nanocomb is shown in Figure 3.15b and the corresponding fast Fourier transformed electron diffraction (FFTED) pattern as the inset. The high resolution TEM image reveals distinct lattice fringe spacing ~ 0.33 nm which corresponds well with (010) plane of CdS. On examining HRTEM examination it is found that no dislocations and planer defects such as stacking faults and twins existed in the nanocoms. The SAED pattern also indicates that the nanocoms are of a highly crystalline nature.
3.6.5 Growth model:

For the growth of micro/nanostructures in vapor deposition system, two mechanisms have been proposed, namely the Vapor-Solid (VS) [15] and Vapor-Liquid-Solid (VLS) [16]. In our experiment, although Au was detected in EDS pattern, VLS mechanism can be ruled out because no metal (Au) particles were found at the structures of the tips of the CdS nanocombs (which is a finger-print of the VLS model). Hence we conclude that the VS mechanism is dominant in this case [17].

Group II-VI semiconductors are found in different morphologies rather than 1D nanostructures such as nanowires and nanorods. Basic understanding of the growth of such morphologies is very important at the scientific level. Asymmetric growth of the II-VI semiconductors is not new to the nano-community. Asymmetrically grown nanoforms such as nanosaws and nanocoms of the ZnO, ZnS and CdSe are well studied by Ma et al. [18]. In examining the nanocombs it was found that they bear a striking similarity to nanobelts which have comb teeth growing on one particular side of the belt. An important property of CdS crystal is the polar surfaces. The most common polar surface is the basal plane. In almost every nanocomb and nanosaw structure examined under TEM, the teeth always grew along the polar (001).
Figure 3.16 Structure model of wurtzite Zn/CdS. The surface is expected to be polar since the (0001) surface is terminated with Zn or Cd and the (000-1) surface is terminated with S. The Zn or Cd surface is likely to be more chemically active than the S surface [19].

The teeth of the nanocomb lie along the [01-10] with their top facets being the same as the nanobelts top and bottom (2-1-10) planes. The two most commonly observed facets for CdS are {2-1-10} and {01-10}, which are non-polar surfaces and have lower energy than the {0001} facets. A detail study of the growth of such novel morphologies is described in brief. Let us consider the wurtzite crystal structures (space group P63mc) with the non specific cations and anions positioned in their respective locations within the unit cell. The (0001) plane, which corresponds to the top of the basal plane of the structure, comprises entirely of cations as shown in Figure 3.16. Conversely, the (000-1) plane, which corresponds to bottom basal plane,
comprises entirely of anions. Because of these two crystallographic planes which consist of either all cations or all anions, the oppositely charged ions produce positively charged Cd\(^+(0001)\) and negatively charged S\(^-(000-1)\) polar surfaces. This results in normal dipole moment and spontaneous polarization along the c-axis as well as a divergence in surface energy. These polar surfaces have differing chemical reactivities which may give rise to the growth of the asymmetric comb teeth on the side of the nanobelts, while the other side is straight and smooth. If the nanobelts grow in such a way that the side surface is polar ± (0001), then a secondary growth may occur. If the chemical reactivities of the two polar surfaces are different, then a preferential growth will spontaneously and simultaneously occur at a more chemically active surface, yielding an asymmetric morphology/growth. The Cd terminated polar surface is chemically active, while the S terminated polar surface is relatively inactive, resulting in spontaneous polarization-induced asymmetric (SPA) growth of CdS nanostructures \[18, 20, 21\].

### 3.7 Field emission study:

The field emission current density-applied field (J-E) characteristic of the CdS nanocombs is depicted in Figure 3.17a.

As the field emission behavior is directly dependent on the relative dimensions of the emitter, CdS nanocombs with fine nanospikes are expected to be good field emitters.
Figure 3.17 (a) J-E plot and (b) corresponding Fowler Nordheim (F-N) plot.
The turn-on field, defined as the field required to draw an emission current density of \( \sim 0.1 \mu A/cm^2 \), was found to be \( \sim 0.26 \) V/\( \mu m \). As the applied voltage was increased further, the emission current was found to increase very rapidly and an emission current density of \( \sim 14.6 \mu A/cm^2 \) is drawn at an applied field of \( \sim 0.65 \) V/\( \mu m \). The observed value of turn-on field is much superior to values reported for CdS nanostructures by other researchers as mentioned in Table 1[1, 3-6, 22].

Table 3.1 Turn-on field values of CdS and ZnO nanostructures reported in the literature.

<table>
<thead>
<tr>
<th>Material</th>
<th>Morphology</th>
<th>Turn on field / V( \mu m^{-1} ) (for ( \sim 0.1\mu A/cm^2 ))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS</td>
<td>Nanocombs</td>
<td>0.26</td>
<td>Present work</td>
</tr>
<tr>
<td>CdS</td>
<td>Aligned Nanowires</td>
<td>0.68</td>
<td>1</td>
</tr>
<tr>
<td>CdS</td>
<td>Quasi aligned and Aligned Nanowires array</td>
<td>8.9, 7.8</td>
<td>3</td>
</tr>
<tr>
<td>CdS</td>
<td>Nanotubes</td>
<td>1.4</td>
<td>4</td>
</tr>
<tr>
<td>CdS</td>
<td>Multipods</td>
<td>7.2</td>
<td>22</td>
</tr>
<tr>
<td>ZnO</td>
<td>Nanowires</td>
<td>6.0</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Nanorods</td>
<td>4.1</td>
<td>6</td>
</tr>
</tbody>
</table>
3.7.1 Possible reasons for observation of low turn-on field:

The lowest value of the observed turn-on field is attributed to the three essential factors.

1) CdS is a mid band gap semiconductor (2.4 eV) as compared to ZnO (3.7 eV), it is expected that the valence band electrons would tunnel out at a lower applied field than that required for the valence band electrons of ZnO.

2) the reduced screening effect in case of the CdS nanocombs due to sufficient spacing between the emitters

3) nanometric dimension of the CdS nanocombs.

In the present case, the current density J is estimated by considering the entire area (1 cm²) of the emitter. The Fowler-Nordheim (F-N) plot i.e. In (J/E²) versus (1/E), derived from the observed J-E characteristic, is shown in Figure 3.17b. The F-N plot shows an overall linear behavior with a decrease in the slope (saturation tendency) in the high applied field range. In present case nanocombs have multiple emitters/spikes with variation in tip diameter hence, the average effect is seen to be linear F-N plot. Such a type of F-N plot exhibiting a tendency toward saturation at a high applied field is consistent with previous reported results [3, 8].

The I-t plot recorded at a base pressure of 1 x 10⁻⁸ mbar is shown in Figure 3.18. The emission current stability of the CdS nanocombs emitter has been investigated at the preset current value of ~ 1 μA and ~ 5 μA. The emission current in both the cases increases initially and stabilizes later on. This can be attributed to the preconditioning of the emitter, as the field emission is a surface sensitive phenomenon and it requires preconditioning by removal of the adsorbs species. The average emission current is seen to be stable over the duration of the measurement, characterized by fluctuations in the form of “spikes”. The appearance of the “spikes” in
the emission current is attributed to the adsorption, desorption, and migration of the residual gas molecules on the emitter surface. The striking feature of the field emission behavior of the CdS nanocombs emitter is that the average emission current remains nearly constant over the entire duration and shows no signs of degradation. The relative stability of the field emission current is expected to be related to the good contact between the Au/Si substrate and the CdS nanocombs. This is a very remarkable feature, particularly from the application point of view as an electron source. Typical field emission images, captured at different applied fields of \( \sim 0.3 \) and \( \sim 0.6 \, \text{V/\mu m} \), are shown in Figure 3.19a,b. The images show a number of tiny spots, corresponding to the emission from most protruding CdS nanocombs. The temporal changes in the intensity of the spots are observed to be commensurate with the emission current fluctuation as seen in the I-t plot.

![I-t plots of the CdS nanocombs](image)

Figure 3.18 I-t plots of the CdS nanocombs taken for the different presets of emission current.
Figure 3.19 Field emission images of CdS nanocombs captured at two different emission current densities.
3.7.2 Photo-sensitive field emission study:

In order to exploit its photoconductivity, we performed photo-sensitive field emission studies by exposing the cathode to a constant intensity of incident light. A cathode was illuminated from 'front side' by keeping a halogen lamp (1300 W/m²) at a distance of ~10 cm for these investigations. The intensity of incident light was calibrated using a photocell and was found to be ~ 80 W/m², at the cathode surface. A plot of the photo-sensitive field emission current versus time is shown in Figure 3.20a. It is seen that the emission current level increases suddenly in the presence of light and it rapidly decreases to the original set value as the lamp is switched off. The rise in the current level is seen to be five times the initial preset value. This light-induced effect on field emission current is observed to be reproducible.

The observed photosensitivity can be attributed to the electrical photoconductivity resulting from the photo induced electrons i.e., electrons from the valence band which are excited into the conduction band, creating additional charge carrier, thus increasing the photoconductivity. Whenever a material has an increase in the number density of electrons in the conduction band due to excitations, the conductivity of that material also increases, as seen in the linear equation for conductivity,

\[ \sigma = n e \mu_e \text{(Ω·m)}^{-1} \]

Where \( n \) is the number density of electrons in the conduction band, \( e \) is the charge of the electrons, and \( \mu_e \) is the electron mobility.

For these electrons to reach the conduction band, the semiconductor must have sufficiently narrow band gap. CdS has a band gap (Eg = 2.4 eV), which puts the excitation wavelength at 520 nm [23]. For higher value of the emission current (~ 10 µA) a photo-sensitive field emission characteristic is also obtained, and is depicted in the Figure 3.20b.
Figure 3.20 Photo-switching behavior of the CdS nanocombs at preset current (a) ~ 1 μA and (b) ~ 10 μA.
A J-E plot with and without light illumination is shown in Figure 3.21 which indicates the effect of illumination on the emission current.

![J-E plot diagram](image)

Figure 3.21 J-E plots of CdS nanocombs with and without light illumination.

The enhanced values of current densities and turn-on fields are mentioned in Table 2. The detailed photo-sensitive field emission mechanism is shown in Figure 3.22. The mechanism indicates that on continuous illumination of the cathode, electrons from the valence band are excited into the conduction band, which contribute to the field emission, significantly increasing the current.
Table 3.2 Field emission performance of CdS nanocombs without and with light illumination.

<table>
<thead>
<tr>
<th>Emitter</th>
<th>Mode of operation</th>
<th>Turn-on field / V_\text{\mu m}^{-1} (for \sim 0.1 \mu A/cm\text{\textsuperscript{2}})</th>
<th>Maximum current density (\mu A/cm\text{\textsuperscript{2}}) (at an field \sim 0.65 V/\mu m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS nanocombs</td>
<td>Without illumination</td>
<td>0.26</td>
<td>14.6</td>
</tr>
<tr>
<td></td>
<td>With illumination</td>
<td>0.24</td>
<td>26.9</td>
</tr>
</tbody>
</table>

Very recently we investigated the photo induced field emission properties of Sn doped ZnO nanowires [24]. The observed photo switching properties of the CdS nanocombs suggest the suitability of the material for device applications and for pulsed electron beam technology.

Figure 3.22 Schematic of photo-sensitive field emission mechanism.
3.8 Effect of the local heating on field emission current due to photo-irradiation:

The chromatic (visible) halogen light source was used for the photo-enhanced field emission experiments. The possibility of contribution of the surface temperature in the photo-enhanced field emission current is excluded.

For thus, l-t measurements were carried out for long duration (~ 82 min) by keeping the light source ON. As depicted in Figure 3.23 it was clear that the photo-enhanced value of the current was stable for the entire duration of the measurement. The observed photo-switching phenomenon was very fast.

Even if there is a small rise in the surface temperature, field emission is known to be insensitive to such a rise. Had there been any such contribution, the fall time of the current (Figure 3.23) has to be large since the specimen will be cooled slowly in the vacuum ambiance.

![Figure 3.23 l-t plot during light ON and OFF mode with long exposure of visible light (~ 82 min).](image)
3.9 Discussion on photo-sensitive field emission and Photoconductive properties of CdS:

Plots of photosensitive field emission current versus time are shown in Figure 3.24. It is clear from Figure 3.24a that the response time is very fast, with typical rise time of 0.05 s (50 ms) whereas Figure 3.24b indicates the decay time of 2.5 s. It is quite certain that the rise time is shorter than the decay time i.e., rate of recombination is not same to the rate generation of electron hole pair, which is the good overall agreement with literature data [25, 26].

Hence, the observed photo-sensitive field emission results can therefore, be attributed to the photoconductivity of CdS.

Also, the PL result shows that the defect states originating across the band gap of CdS due absence of S or excess of Cd are less. As a result, probability of electron hole pair generation and recombination occur across the band gap of CdS.
3.10 Conclusion:

1) For the growth of controlled CdS nanoforms various parameters such as catalyst thickness, Ar pressure, position of the substrates etc. are varied and under optimized condition synthesis of CdS nanocombs, has been carried out.

2) Field emission studies show CdS nanocombs as a suitable candidate for its use as a cold electron source with very low turn-on field \(\sim 0.26\) V/\(\mu\)m (current density \(\sim 0.1\mu\)A/cm\(^2\)).

3) On illumination, rise in the emission current is about five times the preset current value, which is very remarkable. The switching behavior is found to be quite reproducible and the enhancement in the emission current upon illumination is attributable to the photoconductivity of CdS.
4) A good correlation between the PL, photo-sensitive field emission and photoconductive properties of the CdS nanocoms is found.
Chapter III

References:


