Langmuir–Blodgett (LB) film of Cadmium arachidate and CdS nanostructures in the LB matrix

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Outline of the present chapter

In this present chapter we have studied the metal salts of fatty acids as short length molecular templates to explore the specific properties of the molecule that can be used to prepare nano structure materials. A detailed study was performed to understand the structural properties as well as chemical modification due to the formation of nano structure inside the organic matrix. We have prepared cadmium sulphide (CdS) nanostructures in cadmium arachidate LB matrix and the structural modifications were studied in detail with the help of a novel technique.

LB multilayers are suitable precursors for the growth of semiconducting nanostuctures within the nanometric inter layer spacing through post deposition treatments [54—60]. It was shown that by exposing a cadmium arachidate (CdA) LB film in $H_2S$ environment CdS nanostructures can be formed [54,56]. There is a fairly large amount of literature where different aspects of CdS-fatty acid LB systems have been discussed regarding growth and organization of nanoclusters within the LB matrix. Several early papers describe these nanoclusters as nanoparticles [56—58]. Whereas, more recent publications claims they are quasi two dimensional sheets [54,59,60]. It is observed that different investigations with apparently similar LB films demonstrate different degree of modification on sulfidation [54,59—61]. It is also observed that larger exposure of $H_2S$ is required for thicker LB films for saturation of reaction [61]. It therefore indicates that initial structures of the LB films have control over the nature of CdS formation and structural modifications in these films. One important point that seems to be missing in the literature is the generated pressure by the formation of CdS in the films and its expected outcome. Therefore to understand the
nature of pressure induced changes and their correlation with the initial structure, it is necessary to investigate CdS formation in LB films grown with different initial compactness. It was observed that the nature and the extent of the changes depend on the initial mechanical strength or compactness of the concerned structure [114]. It is known that LB films grow with defects and the nature of which depends on various factors like substrate philicity, pH and temperature of the subphase, surface pressure and dipping speed. However, lack of precise control over these parameters can result in statistically similar but microscopically different morphology in apparently identical preparation conditions. With this motivation we have studied the sulfidation in cadmium arachidate LB films that are grown at different surface pressures as a parameter to control the film morphology. Our results from AFM, X-ray reflectivity, TEM, and XPS suggest that on sulfidation there is always a partial chemical conversion and three dimensional CdS nanoparticles are formed in the LB matrix [114]. For a compact LB film layered structure partially remains intact after sulfidation, whereas, in a relatively non-compact film the effect of expansion is more dramatic and different from that of the compact one.

Therefore, it is important to note that there are important issues such as the kinetics of CdS formation, growth and organization of nanoclusters within the LB matrix and the over-all structure of the resulting composite multilayers that need to be addressed properly. These issues have important technological implications for the practical use of these nanocomposite systems in novel nanostructured devices. We have employed a novel technique through analysis of differential charging in X-ray photoelectron spectroscopy (XPS) for the study of structural aspect of multilayer LB films of cadmium arachidate deposited on silicon substrate [116]. For insulating samples, when a photon creates a photoelectron, a net positive charge is left behind. These positive charges accumulate over the surface as the electron current flow into the insulator is insufficient to compensate for the electron loss. This causes differential charging which is often regarded as a problem in X-ray photoelectron spectroscopy (XPS) studies, especially for insulating or partially conducting samples [123]. We have used this differential charging to study the mono and multilayer Langmuir-
4.1. A technique to characterize the LB film: differential charging in XPS

Blodgett (LB) films of cadmium arachidate on silicon substrate [116,117]. Analyzing the differential charging for multilayer films with the help of angle-dependent XPS measurements structural information was extracted. A model has been proposed for the detail charging analysis. In the following sections the details of the developed technique and its use to characterize the LB films before and after sulfidation are discussed.

4.1 A technique to characterize the LB film: differential charging in XPS

4.1.1 Introduction

X-ray photoelectron spectroscopy (XPS) is a powerful surface analytical tool, providing information on the chemical composition of surfaces and interfacial layers. The technique is based on illumination of the sample surface with X-rays and analysis of the photoelectrons ejected from the surface, thereby determining the identity and chemical states of the atoms located on the surface and a few nanometers below it, depending on the inelastic mean free path ($\lambda$) of the ejected electrons through the material. For insulating samples when photon creates a photoelectron a net positive charge is left behind. These positive charges accumulate over the surface because the electron current flow into the insulator is insufficient to compensate the electron loss. The charging is commonly considered as an experimental obstacle to the accurate determination of the binding energies in XPS measurement of poorly conducting sample surface, and various instrumental techniques [123] have been developed to overcome it. Electron flood gun, which is a continuous source of low energy electrons, is commonly used for the neutralization of these excess positive charges, which under certain circumstances, over compensates the sample surface and may even cause negative charging. This can be controlled by tuning electron flood conditions [181]. This technique has been shown to yield chemical, physical and structural information of the samples. Lau and his co-workers [182–187] have published a number of articles
A technique to characterize the LB film: differential charging in XPS

dealing with various aspects of the use of the surface charging for extracting structural and/or electrical properties of ultrathin dielectric films on semiconductors. Elegant use of surface charging for lateral differentiation of mesoscopic structure and for depth profiling in 1 – 10 nm films have been reported [188, 189] in the literature. Instead of using the negative charging, useful information can also be extracted by analysis of positively charged surfaces. The increasing use of positive charging effect to provide sample information is reflected in extensive works of many authors [190–196]. Positive charging can be controlled by an external sample bias while recording the spectrum [190–201]. Dubey and his co-workers [195, 196] have applied this approach to the important area of self-assembled monolayers. The authors used positive and negative biasing of the samples to distinguish between the monolayer and multilayer organic films.

Although the differential charging is often regarded as a problem in X-ray photoelectron spectroscopy (XPS) studies, it is possible to exploit this phenomenon to get useful information about the sample. An attempt is made here to use this differential charging to study the mono and multilayer Langmuir–Blodgett (LB) films of cadmium arachidate on silicon substrate [116]. As a results of differential charging a potential gradient is established on the surface. This potential gradient can be in-plane or out-of-plane depending upon the nature of the sample surface. If we have a multilayer structure like LB films, then it is possible to have vertical potential gradient through the sample as the LB film is insulating in nature. On the other hand, it is possible to probe the vertical variation of a sample by angle-dependent XPS measurements as discussed earlier. So we can make use of this vertical differential charging for structural aspects of organic multilayers with the help of detail angle-dependent XPS measurements of differential charging [116]. The surface potential was probed by measuring XPS line shift with respect to their neutral positions and was found to have correlation with the thickness of the films. No differential charging was observed in the mono layer LB film where there was only one layer of cadmium head group. Significant differential charging was observed for multilayer films, the total charging
as well as the differential charging in these films increase with increasing number of layers.

4.1.2 Experimental

A set of LB film from Monolayer to different multilayers of cadmium arachidate (CdA) were prepared by the conventional LB deposition technique using a KSV 5000 instrument. Arachidic acid \((CH_3(CH_2)_{18}COOH, \text{Sigma, 99%})\) monolayer was spread from a chloroform (Aldrich, 99%) solution in a Langmuir trough on Milli-Q water (resistivity 18.2 \(\text{MO} \cdot \text{cm}\)) containing cadmium chloride (Loba Chemie, 99%). For LB deposition, pH of the water subphase containing \(5 \times 10^{-4} M \text{CdCl}_2\) was maintained at \(6.0 \pm 0.2\) by sodium bicarbonate (Merck, 98%) at room temperature. After preparation, the monolayer was allowed to equilibrate with the sub-phase prior to compression for about 10 minutes. Subsequently, the monolayer was slowly compressed with a constant barrier speed of 3 mm/min until the surface pressure needed for the transfer was reached. The monolayer was kept at constant pressure for 5 min in order to facilitate relaxation. The monolayer was transferred onto a substrate at a surface pressure of 30 mN/m and a transfer speed of 1.5 mm/min.

The substrates for the LB films were Si (100) wafers that were first cleaned in an ultrasonic bath with chloroform for several minutes and then were hydrophilized according to the RCA cleaning procedure by boiling the substrate in a solution of ammonium hydroxide (Merck, 98%), hydrogen peroxide (Merck, 98%) and Milli-Q water \((H_2O : NH_4OH : H_2O_2 = 2:1:1\) by volume) for 10 – 12 min. Immediately after a final rinsing with water, the silicon wafers were placed into the trough and the LB deposition was started.

XPS measurements were performed with an Omicron Multiprobe (Omicron NanoTechnology, UK) spectrometer fitted with an EA125 hemispherical analyzer and a monochromatized Al\( K\alpha (1486.6 \text{ eV})\) source. All data were collected at pass energy 40 eV with analyzer angular acceptance \(\pm 1^\circ\). In normal emission geometry, the sample accepts X-rays at \(10^\circ\) with respect to its surface plane. Keeping the source and the analyzer fixed we can rotate the sample to change the emission angle
4.1. A technique to characterize the LB film: differential charging in XPS

(take-off angle). By this technique a set of angle-dependent measurements were carried out at various take-off angles (with respect to the sample surface) from 90° to 20°. There were some angle-dependent instrumental factors, which shift the peak position towards higher binding energy upto about 0.25 eV at grazing angles. The peak positions were found to vary as the sine of incident angles and were corrected for this instrumental factor. For the study of the bias induced changes of the spectra an external dc electrical bias in the range of +30V to -30V was applied to the samples. The background correction of the data was done by Shirley [169] method. The curve fitting of the core XPS lines were carried out using Gaussian–Lorentzian sum (GL) functions.

To measure the bilayer separation and the thickness of the films X-ray reflectivity (XRR) measurements were performed using an X-ray Diffractometer (D8 Discover, Bruker AXS) with CuKα radiation (λ = 0.154 nm). The periodic density distributions of the layered structure of the LB films are determined by fitting the data to a model based on Parratt formalism [150].

4.1.3 Results and discussions

Quantitative analysis by XPS

First, the detailed quantitative analysis of mono and multilayer LB film of cadmium arachidate were performed by X-ray photoelectron spectroscopy. Cd3d$_{5/2}$ and C1s core level spectra for the single, 3, 5, 7, and 9-layer LB films of cadmium arachidate on silicon substrate were collected at normal take-off angle. The positions and line shapes for these five films were different as shown in figure 4.1.1. Figure 4.1.1-Ia clearly shows that there is no asymmetry of Cd3d$_{5/2}$ peak of single layer LB film as it was fitted well with a single GL function. On the other hand peaks were broadened for 3-layer (figure 4.1.1-Ib), 5-layer (figure 4.1.1-Ic), 7-layer (figure 4.1.1-Id) and 9-layer (figure 4.1.1-Ie) LB films and the fitting requires at least two GL functions.

The C1s XPS spectrum of mono and multilayer LB films of cadmium arachidate is shown in figure 4.1.1-II. There are two peaks in the C1s spectra for all the films,
4.1. A technique to characterize the LB film: differential charging in XPS

![Figure 4.1.1](image)

Figure 4.1.1: Normal take–off angle XPS of $Cd_{3d}^{5/2}$ and $C_{1s}$ core level lines measured for (a) single layer, (b) 3-layer, (c) 5-layer, (d) 7-layer, and (e) 9-layer LB film of cadmium arachidate on silicon substrate.
a strong peak at lower binding energy (around 286.5 eV) corresponding to \( CH_2 \) and \( CH_3 \) carbon atoms and a very weak peak at higher binding energy (around 290 eV) corresponding to the carboxyl carbon atoms of the arachidate chains. As the intensity of the higher binding energy peak is very low, the detail analysis of that peak was not performed for the present study (peak positions are given in the table 4.1.1). Similar to the \( Cd3d_{5/2} \) spectra, no asymmetry was observed in the spectra of single layer film and the asymmetry arises for multilayer LB films as shown in figure 4.1.1-II.

The asymmetry of multilayer data in figure 4.1.1 may be interpreted in terms of multiple chemical environments or due to the presence of differential charging. Careful study of the spectra as a function of X-ray intensity or as a function of electron flood conditions would generally distinguish between the chemically shifted and charging shifted peaks. The chemically shifted peaks should always maintain a constant separation, whereas the charging shifted peaks should merge at a suitable flood current. Using electron flood gun we have observed that these peak asymmetries arise due to sample charging. \( Cd3d_{5/2} \) core level lines of the 3-layer CdA LB film have been measured at 50° take-off angle at different flooding conditions. Figure 4.1.2 shows that the charging asymmetry gradually disappears at increasing electron flux direction. This confirmed that the peak asymmetry in the multilayer LB film is merely due to the differential charging in XPS. Later, we will investigate the nature and cause of differential charging and will make use of it in detail.

Before going to the details of the charging analysis, elementary quantification has been made from XPS spectra of \( Cd3d_{5/2} \) and \( C1s \) at normal take-off angle for all the films. The X-ray photoionization cross sections are different for different elements. To normalize the XPS peak intensity, atomic sensitivity factor (ASF) [124] of 0.296 and 3.444 were used for carbon and cadmium respectively. The obtained atomic ratios of carbon to cadmium for all the films are shown in table 4.1.2. These values are in close agreement with the theoretical value (40:1) and to those reported by Ohnishi et al [202]. The observed difference of our results with the theoretical value may arise due to the chain orientation of the LB films.
Table 4.1.1: Position and relative intensity of two fitted components of Cd3d$_{5/2}$ and C1s spectra for mono and multilayer LB films. The last column shows the binding energy (BE) of the carboxyl carbon.

<table>
<thead>
<tr>
<th>Number of layer</th>
<th>Position of low BE peak (eV)</th>
<th>Position of high BE peak (eV)</th>
<th>Relative intensity of low BE peak (%)</th>
<th>Relative intensity of high BE peak (%)</th>
<th>BE of carboxyl carbon (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mono layer</td>
<td>Cd3d$_{5/2}$: 406.3 285.5</td>
<td>C1s: 405.8 285.5</td>
<td>100.0</td>
<td>100.0</td>
<td>289.2</td>
</tr>
<tr>
<td>3-layer</td>
<td>Cd3d$_{5/2}$: 405.8 285.3</td>
<td>C1s: 406.9 286.3</td>
<td>37.2</td>
<td>10.2</td>
<td>289.8</td>
</tr>
<tr>
<td>5-layer</td>
<td>Cd3d$_{5/2}$: 405.8 285.5</td>
<td>C1s: 407.3 286.7</td>
<td>23.1</td>
<td>11.0</td>
<td>290.2</td>
</tr>
<tr>
<td>7-layer</td>
<td>Cd3d$_{5/2}$: 406.2 285.4</td>
<td>C1s: 407.8 287.2</td>
<td>10.8</td>
<td>6.6</td>
<td>290.9</td>
</tr>
<tr>
<td>9-layer</td>
<td>Cd3d$_{5/2}$: 406.0 285.6</td>
<td>C1s: 407.9 287.2</td>
<td>8.3</td>
<td>6.4</td>
<td>290.8</td>
</tr>
</tbody>
</table>
4.1. A technique to characterize the LB film: differential charging in XPS

Figure 4.1.2: $\text{Cd}3d_{5/2}$ core level lines of 3-layer LB film of cadmium arachidate on silicon substrate at different electron flux conditions (electron fluxes indicated in the figure were measured through a grounded sample). In increasing electron flux direction (figure (b) to (d)) the intensity of low binding energy peak increases and that of the higher binding energy peak gradually disappears.

Table 4.1.2: Carbon: cadmium atomic ratio for mono and multilayer LB films.

<table>
<thead>
<tr>
<th>No. of layer</th>
<th>mono layer</th>
<th>3-layer</th>
<th>5-layer</th>
<th>7-layer</th>
<th>9-layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>C:Cd (atomic ratio)</td>
<td>48:1</td>
<td>35:1</td>
<td>37:1</td>
<td>48:1</td>
<td>55:1</td>
</tr>
</tbody>
</table>
Differential charging analysis

We have shown in figure 4.1.1 that the asymmetric peaks (\(Cd3d_{5/2}\) and \(C1s\)) of the multilayer films have been fitted with two components. The positions and relative intensities of the deconvoluted components are shown in table 4.1.1. We have seen that the binding energy and the relative intensity of these components were different for mono and multilayer LB films. Positions of both the components were found to shift towards higher binding energy with increase in number of layers. If we consider the position of higher binding energy component and the difference in binding energy (\(\delta V\)) between the two components as the measure of maximum charging and the differential charging respectively, then the trend suggests that there is a correlation between film thickness and the characteristics of \(Cd3d_{5/2}\) and \(C1s\) core level lines. The increase in film thickness leads to differential charging and consequently, a significant shift and broadening of the spectral lines were observed. In the following discussion it will be shown that the peak shift and the variation in the line shape are due to vertical differential charging of multilayer LB films. For the single layer LB film there was no asymmetry in \(Cd3d_{5/2}\) and \(C1s\) peaks, which indicates that there was no differential charging in this sample. However, the higher binding energy position for both the peaks compared to their neutral positions suggest uniform sample charging (non differential) in the single layer LB films. Analysis of \(Si2p\) peak of \(SiO_2\) (not shown) shows that there was charging in the oxide layer of the substrate. The observed difference in binding energy of \(Si2p\) peaks between silicon metal and \(SiO_2\) was about 3.6 eV. Whereas the true chemical difference in the binding energies is 3.0 ± 0.2 eV for 1 – 4 nm oxide layer [203]. The additional shift (0.6 eV) appears due to the charging of \(SiO_2\) layer. As the cadmium layer of the monolayer LB film is in direct contact with the \(SiO_2\) layer, the shift of the \(Cd3d_{5/2}\) peak may be attributed to the induced charging of the former by the later [198].

The binding energy difference (\(\delta V\)) and the positions of higher binding energy peak as a function of number of LB layers is shown in figure 4.1.3. It can be observed from the figure that the position of the higher binding energy peak shifts linearly
4.1. A technique to characterize the LB film: differential charging in XPS

Figure 4.1.3: Positions of higher binding energy peaks as functions of number of layers for (a) \( Cd^{3d_{5/2}} \) and (b) C1s. Binding energy difference (\( \delta V \)) between lower and higher energy peaks as functions of number of layers for (c) \( Cd^{3d_{5/2}} \) and (d) C1s. For single layer films \( \delta V \) is considered to be zero. The fitted lines are guide to the eyes.
with the number of layers for both $\text{Cd}_3\text{d}_{5/2}$ (figure 4.1.3a) and C1s (figure 4.1.3b) peaks and the binding energy difference ($\delta V$) shows non-linear behavior as shown in figure 4.1.3c and 4.1.3d. The linear behavior of maximum charging shift can also be explained in terms of capacitance of a parallel plate capacitor [193]. The potential $V$ developed in a layer as a result of charging can be explained as $V = \frac{Q}{C} = \frac{Q}{\varepsilon d}$, where $Q$ defines the accumulated charge on the layer of capacitance $C$, $\varepsilon$ is the permittivity of the layer, and $d$ is the film thickness (proportional to the number of layer). Though it is not possible to calculate the quantity of the accumulated charge in the film, a general trend of inverse dependence of capacitance with number of layers can be observed in agreement with Roberts et al [204]. The behaviour of $\delta V$ (figure 4.1.3c, 4.1.3d) indicates that the differential charging tend to saturate with number of LB layers. This can be substantiated by the behavior of the intensity ratio of the two differentially charged peaks as a function of number of layers (figure 4.1.1). The lowering of the above ratio with increase of number of layers together with saturation of $\delta V$ indicates that these systems can not maintain differential charging beyond a critical quantity.

Sample biasing during XPS measurements: nature of differential charging

As we have mentioned earlier, during photoemission, electrons are emitted from the sample and these electrons are replenished via the ground connection. However, for samples with low electrical conductivity, a net surface positive charge develops because of a difference between the rate of photoemission and rate of replenishment of the electrons. However, some of the surface charging may be neutralized by stray electrons within the vacuum chamber originating from the ion gauge(s). Electron compensation or neutralization of the film regions lying closer to the surface is easier compared to the regions physically further from the sample surface. This leads to differential charging in the same species depending on the distance of such regions from the sample surface. This differential charging can be amplified or reduced by external biasing to understand the reason behind the cause and/or nature of differential charging.
Mono and multilayer films were studied with positive and negative bias applied to the sample in the range of $-30\text{V}$ to $+30\text{V}$. The variations of $Cd3d_{5/2}$ and $C1s$ core level lines of a 7-layer LB film with the application of sample bias are shown in figure 4.1.4 as a typical case. The $Cd3d_{5/2}$ line measured under normal conditions (grounded sample, figure 4.1.4-Ib) shows asymmetry with well-defined shoulder on low binding energy side. The application of $-30\text{V}$ dc bias to the sample causes the $Cd3d_{5/2}$ peak to broaden, shown in figure 4.1.4-Ia. This can be attributed to the presence of overlapping peaks, the intensity and position of those would vary according to the amount of surface charging. Whereas the application of $+30\text{V}$ positive bias causes these two peaks to nearly merge into a single peak as shown in figure 4.1.4-Ic. This indicates that the differential charging can be removed by the application of positive bias to the sample. Similar behaviours were observed for $C1s$ peaks as shown in figure 4.1.4-II. The detailed variation of the binding energy difference ($\delta V$) with the external bias voltage for $Cd3d_{5/2}$ and $C1s$ peaks are shown in figure 4.1.5. It is interesting to note that there is no change in line-shape, FWHM or position of $Cd3d_{5/2}$ and $C1s$ peaks for single layer LB films under external bias (not shown). The result shows that there is no differential charging in the single layer LB films, which further supports our assumption that the differential charging appears only in the multilayer films.

It was observed that partial neutralization of samples was possible due to the presence of stray electrons (originating from the ion gauge, etc.) in a vacuum chamber [192,195,196,198]. On the application of a negative bias, stray electrons are repelled from the sample which increases the differential charging (increase in $\delta V$). When positive bias is applied, stray electrons are attracted to the surface and partially compensate the loss of electrons from the films, thereby decreasing differential charging as shown in figure 4.1.5. Variation of secondary electrons generated within the samples upon X-ray exposure due to the change of sample bias may be another source of partial neutralization [192].
4.1. A technique to characterize the LB film: differential charging in XPS

Figure 4.1.4: XPS $Cd3d_{5/2}$ (panel I) and $C1s$ (panel II) core level lines of 7-layer LB film on silicon substrate measured with the application of electrical bias to the sample. Three typical cases for (a) $-30V$, (b) $0V$ and (c) $-30V$ bias conditions are shown.

Figure 4.1.5: Binding energy difference ($\delta V$) vs. the bias voltage for $Cd3d_{5/2}$ and $C1s$ lines of 7-layer LB film of cadmium arachidate on silicon substrate. The fitted lines are given as guide to eyes.
4.1. A technique to characterize the LB film: differential charging in XPS

Angle-dependent XPS measurements: Structural aspects of LB multilayers

The $Cd3d_{5/2}$ and $C1s$ core level lines were studied for all the samples at different take-off angles (90° to 20°). Figure 4.1.6 shows the $Cd3d_{5/2}$ spectra for mono layer, 3-layer and 5-layer films at different take-off angles. For the single layer LB film (figure 4.1.6a), peaks at all angles were fitted with a single GL peak. The peak positions and widths were found to be identical for all take-off angles. This implies that there was no differential charging along the depth for single layer LB films. For multilayer films, peaks were more broadened at grazing angles and in order to fit the data a combination of at least two GL functions were required. For all the films studied, the intensity of the lower binding energy peaks were found to increase at grazing angles along with a gradual shift of the positions towards the lower binding energy side. This implies that there must be a vertical differential charging in the multilayer films.

It was observed from figure 4.1.6 that the intensity ratio of lower binding energy to higher binding energy peaks increases with take-off angle ($\theta$) which indicates that the contribution of the lower binding energy peaks comes from the upper part of the sample [125]. This may be explained in terms of neutralization due to stray electrons as has been discussed in the previous section. In this situation electron compensation or neutralization of the film regions lying closer to the vacuum surface is easier compared to that for regions away from the surface. The effect become more important as there is an insulating $SiO_2$ layer on the substrate which prevents the electron supply from the ground. In support of this observation we have taken the angle-dependent data of a 5-layer LB film keeping the sample at floating condition (sample detached from ground). In this situation the peaks have been shifted to higher binding energy as expected but the differential charging have the similar behavior as that of the grounded samples as shown in figure 4.1.7.

The asymmetry of the $C1s$ peaks for multilayer samples were less compared to those of $Cd3d_{5/2}$ peaks as shown in figure 4.1.1-II. Although the behavior of the high
4.1. A technique to characterize the LB film: differential charging in XPS

Figure 4.1.6: Cd3d5/2 core level XPS lines measured for (a) single layer, (b) 3-layer and (c) 5-layer LB film of cadmium arachidate on silicon substrate at different take-off angles ($\theta$).
4.1. A technique to characterize the LB film: differential charging in XPS

Figure 4.1.7: Cd\textit{3d}_{5/2} core level XPS lines measured for 5-layers LB film at various take-off angles (\(\theta\)) keeping the sample at floating condition (ground connection open). Peaks shifts to higher binding energy due to charging. All the peaks have been aligned to the position of the grounded sample for comparison.

binding energy to low binding energy peak intensity ratio is not identical to that of Cd\textit{3d}_{5/2} peaks, there is a clear trend of lowering of the ratio towards grazing angles. In LB films there are discrete layers of cadmium ions embedded in the continuous hydrocarbon stacks. The observation indicates that the differential charging for both cadmium and carbon layers are similar in nature with upper part of the film being less charged. The comparison of the C1s and Cd\textit{3d}_{5/2} multilayer data with respect to the structure of the LB films suggests that the discrete cadmium layers separated by insulating hydrocarbon stacks are likely to have higher differential charging. The prominent differential charging behaviour of the cadmium layers have been utilized for the determination of the structural aspects of the multilayer films as has been discussed below.

Let us consider a hypothetical layered structure where two infinitesimally thin layers (marked as layer 1 and layer 2) are embedded in the homogeneous multilayer stacks as shown in figure 4.1.8, then the photoelectron intensity from infinitesimally thin embedded homogeneous layer 1 and 2 can be written as [125,205] (discussed
4.1. A technique to characterize the LB film: differential charging in XPS

Nature of

Intensity ratio

Take-off angle (θ)

Figure 4.1.8: A hypothetical layer structures where two infinitesimally thin layers (in red colour) are embedded in the homogeneous multilayer stacks (left) and general trend of intensity ratio of upper layer to that of lower layer with take-off angles (right).

earlier in chapter 2)

\( I(\theta, t_1) = KD(E, \theta) n_E \sigma_E \exp\left(\frac{-t_1}{\lambda \sin \theta}\right) \)  \hspace{1cm} (4.1.1)

\( I(\theta, t_2) = KD(E, \theta) n_E \sigma_E \exp\left(\frac{-t_2}{\lambda \sin \theta}\right) \)  \hspace{1cm} (4.1.2)

Intensity ratio between the photoelectron of upper thin layer to that of lower thin layer can be written as

\[
\frac{I(\theta, t_1)}{I(\theta, t_2)} \propto \exp\left(\frac{t_2 - t_1}{\lambda \sin \theta}\right)
\]

\[
\Rightarrow I(\theta) \propto \exp\left(\frac{d}{\lambda \sin \theta}\right) \quad (4.1.3)
\]

where \( d = t_2 - t_1 \) is the separation between two layers. The corresponding nature of intensity ratio as a function of electron take-off angles (θ) shows that the intensity of the upper layer increases at the grazing angle as shown in the figure 4.1.8.

As we have mention earlier in chapter 2 that the electron take-off angle (θ) variation gives us an opportunity to probe the out-of-plane structural variation of a sample. We have seen that our multilayer LB films are differentially charges in the
A technique to characterize the LB film: differential charging in XPS

Figure 4.1.9: Schematic of a typical 3-layer LB film of cadmium arachidate on hydrophilic silicon substrate. The solid spheres and the solid lines represent the cadmium head groups and the hydrocarbon tails respectively. $d$ represents bilayer separation.

out-of-plane direction as a result $Cd3d_{5/2}$ peaks are broaden and have been fitted with a two components as discussed earlier.

We have applied the above intensity ratio formula to our multilayer LB films. In the case of 3-layer LB films on hydrophilic substrate, there are two layers of cadmium ions as shown in figure 4.1.9. Following equation 4.1.3 the ratio of intensity of photoelectrons emitted from the upper cadmium layer to that of lower can be expressed as

$$I(\theta) \propto \exp\left(\frac{d}{\lambda_{LB} \sin \theta}\right)$$  \hspace{1cm} (4.1.4)

Where $d$ is the separation between the two cadmium layers and $\lambda_{LB}$ is the attenuation length of photoelectrons from cadmium in the cadmium arachidate LB film. In our case all the multilayer films are differentially charged with upper part of the film being relatively neutral with respect to the lower part. These two charging states give rise to the two distinct peaks for the cadmium spectra.

To describe the intensity ratio of these two peaks we assume that the layer separation $d$ does not represent the physical separation between the two successive cadmium layers, it rather represents the separation between two differentially charged states in the multilayer film. In figure 4.1.10 we have plotted intensity ratio of the two peaks for all the multilayer films. The formula (equation 4.1.4) has been applied to fit the data. Although the data for all the films fits quite well, the values
of the parameters obtained from the fits (fitting not shown) appear to be grossly unphysical. It may be noted that the LB films normally contains defects and the assumption of the homogeneous cadmium layers separated by definite hydrocarbon layers are unlikely to be strictly valid in this case. To overcome the problem we have applied the stretched exponential function that takes care of a distribution of layer separation [206] and the equation 4.1.4 can be modified as

\[ I(\theta) \propto \exp\left( \frac{d_{\text{eff}}}{\sin \theta} \right)^\gamma \quad : \text{where} \quad d_{\text{eff}} = \frac{d}{\lambda_{LB}} \]  

(4.1.5)

The numerical value of the exponent \( \gamma (0 < \gamma < 1) \) can be correlated with the defects of the films with \( \gamma \) close to zero indicating a defective film and close to unity indicating a defect free one.

It was observed that the two parameters \( d_{\text{eff}} \) and \( \gamma \) were not completely independent for the range of our data. To avoid this ambiguity we have taken a fixed
Table 4.1.3: Comparison of different parameters obtained for the multilayer LB films. \( d \): separation between the two differentially charged cadmium layers according to our model (see text for detail), \( d_{ex} \): obtained separation between the two differentially charged cadmium layers from angle-dependent XPS measurements using our model.

<table>
<thead>
<tr>
<th>Number of layer</th>
<th>3-ML</th>
<th>5-ML</th>
<th>7-ML</th>
<th>9-ML</th>
</tr>
</thead>
<tbody>
<tr>
<td>( d_{model} )</td>
<td>51.0 Å</td>
<td>76.3 Å</td>
<td>105.6 Å</td>
<td>129.8 Å</td>
</tr>
<tr>
<td>( d_{ex} )</td>
<td>51.0 Å</td>
<td>72.5 Å</td>
<td>79.6 Å</td>
<td>86.6 Å</td>
</tr>
</tbody>
</table>

value of \( d_{eff} \) (d from our reflectivity data and \( \lambda \) from literature [205]) to fit the data of the 3–layer LB film. The value of \( \gamma \) (0.31) obtained from the fitting was used as a fixed parameter to extract the effective separation \( d_{eff} \) for all other films. In table 4.1.3, we have compared the obtained values of the parameter \( d \) (represented as \( d_{ex} \) in the table 4.1.3) for all the multilayer films.

In order to correlate the obtained values of \( d \) (separation between two differentially charged peaks) with the physical structure of LB multilayers, a detailed X-ray reflectivity measurements were performed for all the films. XRR data with the fits for mono and multilayer films of CdA along with the electron density profiles are shown in figure 4.1.11. The results indicate that all the LB films used in the present study consist of layered structures as expected.

On the basis of the value of \( d \) (denoted as \( d_{ex} \) in table 4.1.3) in the expression of \( d_{eff} \) obtained from the fitting and the physical structure obtained from the reflectivity fitting, we can model the values of \( d \) as the gap (separation between two differentially charged layers) between the neutral cadmium layer close to the top surface and the average position of all other cadmium layers in the interior of the films as shown in the schematic 4.1.12. These separations (denoted as \( d_{model} \) in the table 4.1.3) for all the multilayer films have been calculated from X-ray reflectivity results and are presented in table 4.1.3. It may be noted that for 3–layer LB films the physical separation between the two cadmium layers \( (d) \) is identical to that of the separation between the two charged layers \( (d_{model}) \) in this model. Our results closely represent the structure of the 5–layer LB film. For the thicker films although the obtained numbers \( (d_{ex}) \) underestimate the calculated values \( (d_{model}) \), the increasing trend of
4.1. A technique to characterize the LB film: differential charging in XPS

Figure 4.1.11: X-ray reflectivity data with respect to the moment transfer ($q_z$) along the normal to the surface with the corresponding fitting of (a) 3-layer, (b) 5-layer and (c) 7-layer, and (d) 9-layer LB film of cadmium arachidate on silicon substrate. The electron density profiles of the corresponding films are shown in their insets.

Figure 4.1.12: Schematic of 5-ML LB film showing the model values ($d$); the gap (separation between two differentially charged layers) between the neutral cadmium layer close to the top surface and the average position of all other cadmium layers in the interior of the films.
4.1. A technique to characterize the LB film: differential charging in XPS

d_{eq} with number of layers follow the expected behaviour. The failure of the present model for thicker films may be attributed to the fact that the defects in the LB films increase with increasing number of layers, whereas we have chosen the value of \( \gamma \), the representative of the film quality, to be constant for all the films as a first approximation in our model. The above method can be applied to have some structural aspects of multilayer organic film within the limit of validation of the model. The method can be really important if we have ultrathin organic film where there is some chemical variation or variation due to differential charging is present.

4.1.4 conclusions

Differential surface charging has been used to derive the information about the thickness and structure of mono and multilayer Langmuir–Blodgett films of cadmium arachidate on silicon substrate. Analysis of \( \text{Cd}^{3d_{5/2}} \) and \( \text{C}1s \) core level line from monolayer normal emission XPS data shows that there is no differential charging in the single layer LB film. Differential charging arises for the multilayers and increases with increasing number of layers. Linear behavior of the maximum charging shift as a function of number of layers can be interpreted in terms of capacitance of a parallel plate capacitor. Saturation of difference between the two deconvoluted peaks \( (\Delta V) \) in the differentially charged films suggests that LB films can not maintain differential charging beyond a critical value. It was found that mono and multilayer LB films cause different responses of XPS characteristics to the sample bias applied during measurements. Both positive and negative biases were found to affect the \( \text{Cd}^{3d_{5/2}} \) and \( \text{C}1s \) line shapes of the multilayer LB films as a result of partial neutralization due to stray electrons in the chamber, whereas for the monolayer film the data was not affected by the application of a dc bias.

In angle–dependent XPS analysis, we have seen that the peak broadening increase at grazing angle i.e. by increasing the surface sensitivity of the sample, indicating a potential gradient in the XPS analyzed volume. The peaks have been deconvoluted into two peaks. The intensity ratio of the lower to the higher binding energy peaks increase at grazing angles which implies that the upper part of the samples were more
neutral with respect to the lower part. It was also demonstrated that the analysis of differential charging with the help of a model can provide structural information of the multilayer LB films.
4.2 Formation of CdS nanostructures in LB matrix; Role of initial morphology

4.2.1 Introduction

Well ordered LB films of cadmium arachidate are extremely useful precursor for the formation of semiconducting nanostructures (CdS nanostructures) by passing the \( H_2S \) gas thorough the sample [114]. In this approach the multilayer structures acts as a template and better control over size and shape of nanoclusters are expected. There are important issues such as the kinetics of CdS formation, growth and organization of nanoclusters within the LB matrix and the overall structure of the resulting composite multilayers that need to be addressed properly. These issues have important technological implications for the practical use of these nanocomposite systems in novel nanostructured devices.

In this section a detailed study was performed to examine the issues like the shape of the CdS clusters, time, and thickness dependence of chemical conversion and to study the correlation between the pre and post sulfidation structure of the LB films on CdS formation, a set of multilayer cadmium arachidate LB films grown with different morphology and thickness have been studied using AFM, TEM, X-ray reflectivity, and XPS. Microscopic evidence of formation of nearly uniform CdS nanoparticles of around 4.5 nm in the LB matrix was observed. In relatively compact films, mount like structures were found to develop due to out-of-plane molecular motion, whereas, for non-compact films, expansion and molecular rearrangement appears to reduce the height non-uniformity and smooth out the surface as a result of sulfidation. Full conversion of cadmium arachidate to CdS was not achieved in the LB matrix even after a long exposure and the time required for conversion was found to be independent of film thickness, both contrary to the earlier observation. A partial conversion of a maximum of around 60% could be achieved in the films of various thickness and compactness indicating that partial survival of the layered structure after sulfidation may be possible in initially compact films.
4.2. Formation of CdS nanostructures in LB matrix; Role of initial morphology

4.2.2 Experimental

LB films of cadmium arachidate (CdA) were prepared by the conventional LB deposition technique using a KSV 5000 instrument as described in the previous section. A set of 5-layer films were prepared at surface pressures 30 mN/m, 20 mN/m, and 40 mN/m referred to as sample A, B, and C respectively to have a sample set with different initial structures and morphologies. A 25-ML and a 3-ML film were also prepared at 30 mN/m for comparison. All the films were exposed to $H_2S$ gas in a closed glass tube for sulfidation reaction to produce cadmium sulphide nanostructures in LB matrix. Surface topography of all the films was studied by AFM (NanoScope IV) in tapping mode. Scans of different areas were performed in constant force mode over several regions of the films. Size of $CdS$ nanoparticles in LB matrices have been estimated from the Transmission electron microscopy (TEM) measurement. For TEM measurement $CdS$ nanoparticles were taken out from LB film by sonication of $H_2S$ treated LB films in chloroform and drop casted on a carbon coated copper grid. The electron microscopy studies were done with a JEOL JEM–2010 microscope operated at 200 KV. To measure the bilayer separation and the thickness of the films, X-ray reflectivity (XRR) measurements were performed using an X-ray diffractometer (D8 Discover, Bruker AXS) with $CuK\alpha$ radiation ($\lambda = 0.154$ nm). The density distributions of the layered structure of the LB films are determined by fitting the data to a model based on Parratt formalism [150]. For chemical analysis of the samples XPS measurements were performed with an Omicron Multiprobe (Omicron NanoTechnology, UK) spectrometer fitted with an EA125 hemispherical analyzer and a monochromatized $AlK\alpha$ (1486.6 eV) source. All data were collected at pass energy 40 eV with analyzer angular acceptance $\pm 1^\circ$. The background correction of the data was done by Shirley method [169]. The curve fitting of the core XPS lines was carried out using Gaussian–Lorentzian sum (GL) functions.
4.2.3 Results and Discussion

Structure and morphology

At first we have studied the surface morphologies of all the films by Atomic Force Microscopy (AFM). Figure 4.2.1 shows AFM topographic images for samples A, B, and C with corresponding line profiles and height distributions in the inset before and after sulfidation. The RMS roughness values obtained from the figures for all the samples are tabulated in table 4.2.1. It is shown in figure 4.2.1a that uniform film with distributed pinhole defects typical of LB films was deposited for sample A. Corresponding height distribution shows that the peak of the distribution was at ~ 70 Å with an asymmetry towards lower heights. Considering the thickness of 5ML LB film to be ~ 125 Å the observed maximum height of ~ 70 Å indicates that the film having a thickness ~ 50 Å, equivalent to the first two monolayers, was deposited with very low defects. Asymmetry towards lower heights indicates increase of defects with increase in number of layers. The RMS roughness for sample A was observed to be 11 Å which indicates that sample A was quite uniform and smooth as expected for a compact LB films.

On the other hand, AFM analysis shows that non-uniform films with larger defects are formed when films are deposited at surface pressures of 20 and 40mN/m for sample B and C as shown in figure 4.2.1c and e respectively. Figure 4.2.1c shows a maze like morphology of high regions separated by low regions for sample B. Surface of sample C mainly shows scattered patches with larger heights as can be observed in figure 4.2.1e. Height distributions for sample B and C show that several different heights are present in these samples (inset of figure 4.2.1c and 4.2.1e). It is observed that maximum height (133 Å) for sample B was comparable to the thickness of 5ML LB film (125 Å). This result indicates that defects start to appear from the first monolayer which means some uncovered regions are present in this case due to the formation of non-compact layer on the subphase at lower pressure during deposition. For sample C the maximum height was ~ 177 Å which is much larger than the thickness of 5ML films. This may be explained in terms of the fact that at
Figure 4.2.1: AFM images of 5-ML LB films of cadmium arachidate on silicon substrate. Figure (a, b), (c, d) and (e, f) represent the surface morphologies of sample A, B and C respectively before and after sulfidation. Line profiles and height distributions of the top surfaces are shown in the inset of the respective figures in the same scale before and after sulfidation for ease of comparison.
higher pressure collapse of monolayer and their staking occurs on the subphase and deposition of such multilayer stacks gives rise to larger heights. The RMS roughness of the sample B and C of 38.6 Å and 43.9 Å respectively are much larger than that of sample A. Above results show that LB films with large defects or free space are formed at 20mN/m and 40mN/m surface pressures.

Changes in the structures and the morphologies of the three films (A, B, C) after reaction with hydrogen sulphide gas was remarkable. The AFM images after sulfidation are shown in figure 4.2.1b, d, and f. The changes in morphologies were different for different films depending on their initial structures. For sample A the position of the peak shifts to slightly lower height with a minute lowering of asymmetry whereas the RMS roughness slightly enhance (12 Å) after sulfidation as shown in figure 4.2.1b. Lowering of peak position and asymmetry indicates that defects in the entire film are reduced due to expansion. It is interesting to note from the line profile of the sulphided film that mount like structures of larger heights have grown as a result of out-of-plane expansion in this film. On the other hand large changes in the morphologies were observed for non-compact samples B and C as there were larger available free space for molecular movements in these films. Two or more prominent height distributions come to a single distribution for these samples and the positions of the peaks move substantially towards lower heights. The RMS roughness values reduce to 14.6 Å and 13.2 Å for the films B and C respectively after

<table>
<thead>
<tr>
<th>Sample</th>
<th>Before sulfidation (Å)</th>
<th>After sulfidation (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>11.0</td>
<td>12.0</td>
</tr>
<tr>
<td>Sample B</td>
<td>38.6</td>
<td>14.6</td>
</tr>
<tr>
<td>Sample C</td>
<td>43.9</td>
<td>13.2</td>
</tr>
</tbody>
</table>
sulfidation. It is clear that sulfidation induced expansion and rearrangement process reduces the height non-uniformity and smooth out the film surfaces in these samples.

In addition to the study of in-plane morphological evolution by AFM, X-ray reflectivity studies have been performed to understand the out-of-plane structures and the interfacial properties of all the films prepared at different conditions before and after sulfidation. The reflectivity profiles (open circles) were fitted using Parratt formalism [150] and the corresponding electron density profiles (edp) are shown in figure 4.2.2 for all the samples. Electron density profile as a function of depth shows (inset of figure 4.2.2a) presence of discrete cadmium layers in the multilayer structure for sample A as expected. Although samples B and C prepared at 20 and 40mN/m surface pressures give somewhat similar reflectivity data (figure 4.2.2c and 4.2.2e) to that of sample A, the electron density profiles obtained from the fittings of the data show step like and lower (compared to sample A) electron densities with little sign of discrete cadmium layers as shown in the inset of the figures. Successive reduction of coverage in these films may give rise to such descending step like edp. We have observed from AFM data that a large part of the surface was uncovered for these samples. Overall lower film density compared to that of sample A may appear due to averaging with these uncovered regions. After reaction with $H_2S$ gas significant changes were observed in the reflectivity profiles as shown in figure 4.2.2b, d and f. Reflectivity was found to decrease rapidly with loss of oscillation for all the samples which indicates increase in interfacial roughness. For sample A the changes in structure was such that the electron density decreases continuously from the first layer with two intermediate high density regions represented by two hump like features in the edp. These higher density regions may appear due to the presence of cadmium head groups in the film. However, precise positions of the high density cadmium head groups cannot be estimated correctly from the present results. At the most it may be speculated that there are two dispersed cadmium layers in the hydrocarbon stacks. No meaningful information regarding the structures of sample B and C after sulfidation was observed from the x-ray reflectivity data, only the step like edps were further smooth, as shown in the insets of figure 4.2.2d and f.
Figure 4.2.2: X-ray reflectivity data with respect to the momentum transfer ($q_z$) along the normal to the surface with the fits for (a) sample A, (b) sample A after sulfidation, (c) sample B, (d) sample B after sulfidation (e) sample C, and (f) sample C after sulfidation. The electron density profiles of the corresponding films are shown in the inset.
4.2. Formation of CdS nanostructures in LB matrix; Role of initial morphology

The total film thicknesses obtained from XRR data before and after sulfidation for all the films are given in table 4.2.2. It was observed that the film thickness decreases after sulfidation for all the samples, however, the reductions were much larger for the films with larger defects indicating larger rearrangement in these films. We have observed from AFM data that the sulfidation smoothes out the film morphology. Generally it is believed that with smoothing out of the top surface, X-ray reflectivity of the films should be better, whereas in this case XRR data was worse and was unable to provide meaningful information regarding the structural changes. To understand the reason, we have to look into the internal structure of LB films. In cadmium arachidate LB films vertically separated cadmium ions in narrow layers are present within the arachidic acid chains. After reaction with \( \text{H}_2\text{S} \), sulphur and hydrogen are added to the system and the metal ions through which the monolayers are connected to one another are detached from the chains. Also the nanometer sized \( \text{CdS} \) clusters are formed in this process [54]. Therefore formation of a new structure is possible as a result of lateral displacement of the molecules related to the additional pressure of particle formation. The smoothing of the films along with the reduction in thickness may be understood in terms of the expansion of the compact vertical cadmium arachidate molecular stacks followed by the occupation of the free space by inclined molecules. As expected, this effect is more prominent for the films prepared at 20mN/m and 40mN/m where large area of the substrates was initially uncovered. This change of internal layered structure may explain the loss of reflectivity in the treated films.

In regards to the formation of \( \text{CdS} \) nanostructures inside the LB matrix it is very important to understand shape and size of the produced nanostructures. The size of \( \text{CdS} \) nanoparticles in LB matrices have been estimated from the TEM measurements. Figure 4.2.3 shows the TEM morphology of \( \text{CdS} \) nanoparticles taken out from the films by sonication of \( \text{H}_2\text{S} \) treated films in chloroform. Corresponding histogram for particle size distributions is given in the inset of the figure. Agglomeration of nearly uniform \( \text{CdS} \) nanoparticles of diameter around 4.5 nm was observed as shown in figure 4.2.3a. Selected area high resolution TEM (figure 4.2.3b) show a inter planner
Table 4.2.2: The total film thickness obtained from XRR data before and after sulfidation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Before sulfidation (Å)</th>
<th>After sulfidation (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>135.7 (Å)</td>
<td>116.5 (Å)</td>
</tr>
<tr>
<td>Sample B</td>
<td>133.3 (Å)</td>
<td>97.7 (Å)</td>
</tr>
<tr>
<td>Sample C</td>
<td>147.7 (Å)</td>
<td>98.4 (Å)</td>
</tr>
</tbody>
</table>

Figure 4.2.3: (a) Transmission electron microscopy (TEM) images of CdS nanoparticles in LB matrix. Corresponding particles size distribution is also shown in the inset. (b) Selected area high resolution TEM shows clear fringes with inter planner spacing of 1.89 ± 0.02 Å which matches [103] planes of hexagonal CdS.
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Spacing of 1.89 ± 0.02 Å which matches with (103) planes of hexagonal CdS. It may be noted that such spherical particles would almost span one bilayer of arachidic acid in LB films. In such case multilayer structures should be destroyed completely after CdS formation if full conversion of cadmium arachidate to CdS is achieved.

XPS study

In order to understand the chemical conversion of Cd ions to CdS, it is necessary to investigate the chemical changes of the LB films after sulfidation. The chemical analysis of the samples before and after sulfidation has been done by XPS. Similar to our earlier observation [116] for multilayer LB films, peak shifting and broadening occurs here due to sample charging in XPS. In figure 4.2.4 and 4.2.5 we have shown the post sulfidation XPS data (pre sulfidation data not shown). Figure 4.2.4 shows S2p data corresponding to the CdS nanoparticles for sample A as a typical case. The S2p spectrum was fitted with single spin-orbit-split doublet, 2p3/2 and 2p1/2, separated by 1.1 eV. Here the S2p1/2 component was assigned half the intensity of the S2p3/2. The peak position of S2p3/2 and Cd3d5/2 at 161.6 eV and 405.6 eV (after charging correction) confirms the formation of CdS [124]. Due to the presence of differential charging the Cd3d5/2 and C1s peaks are fitted with two components as shown in figure 4.2.5.

For quantitative compositional analysis atomic sensitivity factor (ASF) [124] values of 0.296, 3.444 and 0.57 were used for C1s, Cd3d5/2 and S2p respectively. The obtained carbon to cadmium atomic ratios for all the films are shown in table 4.2.3. For Sample A and B this value was close to the theoretical value (40) whereas for Sample C it was somewhat larger which may arise due to the shadowing effect as a result of chain orientation in the film. It may be noted that this number reduces significantly for all the samples after sulfidation, however, for samples that have more defects or free space this reduction was very large. It was observed that C to Cd ratio does not change noticeably due to long storage of the films in the XPS chamber, therefore the change in the ratio should be related to the sulfidation process. Assuming no loss of carbon during the chemical reaction, the reduction of the ratio
Figure 4.2.4: $S_{2p}$ core level line measured for 5-ML LB film (sample A) after sulfidation.

Figure 4.2.5: (a) $Cd3d_{5/2}$ and (b) $C1s$ spectra of sample A after sulfidation. Both the spectra are fitted with two components.
4.2. Formation of CdS nanostructures in LB matrix; Role of initial morphology

Table 4.2.3: Carbon to cadmium and sulfur to cadmium atomic ratios for all multilayers LB films.

<table>
<thead>
<tr>
<th>Samples (sulfidation time within bracket)</th>
<th>Before sulfidation</th>
<th>After sulfidation</th>
<th>Atomic ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>A(15 min)</td>
<td>37.0</td>
<td>30.7</td>
<td>0.62</td>
</tr>
<tr>
<td>A(30 min)</td>
<td>37.0</td>
<td>25.2</td>
<td>0.59</td>
</tr>
<tr>
<td>A(6 hr)</td>
<td>37.0</td>
<td>28.1</td>
<td>0.63</td>
</tr>
<tr>
<td>B(15 min)</td>
<td>46.5</td>
<td>22.9</td>
<td>0.42</td>
</tr>
<tr>
<td>C(15 min)</td>
<td>53.7</td>
<td>27.1</td>
<td>0.54</td>
</tr>
<tr>
<td>25 ML(15 min)</td>
<td>47.6</td>
<td>25.3</td>
<td>0.59</td>
</tr>
<tr>
<td>3 ML(15 min)</td>
<td>35.3</td>
<td>28.4</td>
<td>0.47</td>
</tr>
</tbody>
</table>

may indicate that the CdS particles grown in LB matrix get more exposed to the X-rays compared to the cadmium ions in the pristine LB films. The calculated cadmium to sulfur atomic ratios for all the samples are compared in table 4.2.3. It is interesting to note from the table that this ratio was much less than unity (for stoichiometric CdS) for all the samples which indicates that complete conversion of cadmium arachidate to CdS did not occur in the LB matrix even in films with large defects (B and C). It is also important to note that the conversion does not increase beyond 15 min exposure of H₂S. In table 4.2.3 we have also compared the conversion in a 3-ML and a 25-ML film. One can observe that the percentage of conversion does not change with number of monolayers. Contrary to the earlier observation [61] our results indicate that in LB matrix CdS formation does not depend on film thickness and the reaction completes within 15 min of H₂S exposure with a maximum conversion of around 60% of Cd salt.

It may be noted that in case of well grown compact LB films the presence of about 40% un-reacted salt after sulfidation may maintain the bilayer structure. Therefore in XRR technique samples are assumed to be homogeneous over the probe size, the presence of unmodified regions may lead to misinterpretation of the data. Now
our developed method come into play to overcome the issue with the help of the differential charging in the angle-dependent XPS data of the multilayer system as discussed in the previous section.

4.2.4 Conclusions

Formation of CdS nanoclusters in Cadmium arachidate LB films is known in the literature. However, the shape of the cluster remains an open question in absence of direct microscopic evidence. It was observed earlier that when \( H_2S \) is passed in cadmium arachidate LB films the acid converts completely to \( CdS \) and the conversion depends on thickness or the number of monolayers of the films. As regard the final shape of the LB films it was predicted that films retain layered structures after sulfidation. To re-examine some previous findings regarding the shape of particles, reaction time, conversion fraction and to study the effect of generated pressure in the LB films due to formation of \( CdS \) we have studied the sulfidation of a set of 5-ML cadmium arachidate LB films that are grown at three different subphase pressures of 20, 30 and 40mN/m. To study the thickness dependence of chemical conversion a 3-ML and a 25-ML film are also studied. Uniform surface with distributed pinhole defects with presence of discrete cadmium layers embedded in the multilayer hydrocarbon stacks was observed for LB films prepared at 30mN/m. Whereas patchy and non-uniform morphologies with descending film coverage towards the top surface was observed for the films grown at 20 and 40mN/m subphase pressures. Dramatic changes were observed for all the films after sulfidation. Layered structures of \( H_2S \) treated films get damaged and their thicknesses reduce due to sulfidation. Direct microscopic evidence of formation of nearly uniform \( CdS \) nanoparticles in the LB matrix was observed. In relatively compact films, mound like structures develop due to out of plane motion of the molecules. Whereas for non-compact films expansion and rearrangement appears to reduce the height non-uniformity and smooth out the whole film surface due to sulfidation process. The chemical analysis indicates that the time of conversion of cadmium arachidate to \( CdS \) was short and does not depend on film thickness. A partial conversion of a maximum of around 60
4.2. Formation of CdS nanostructures in LB matrix; Role of initial morphology

% cadmium arachidate to CdS could be achieved in films of various thickness and compactness indicating that in an initially compact film, a partial layered structure may remain unaltered after sulfidation. The presence of unmodified layered structure after sulfidation may lead to misinterpretation of the data as in XRR technique samples are assumed to be homogeneous over the probe size. It is necessary to apply our developed method to have the structural information of the partially modified LB films after sulfidation with the help of the differential charging in the angle-dependent XPS data as discussed in the previous section.
4.3 Application of differential charging characterization method to the modified LB films

4.3.1 Introduction

In the present section differential charging in angle-dependent XPS measurements has been used to investigate the structural changes in multilayer LB films of cadmium arachidate on silicon substrate deposited at different conditions before and after sulfidation. In this study XPS results were complemented with XRR and AFM studies to observe the differences in the structure and morphology in the light of differential charging in XPS.

As we have discussed earlier that the differential charging in XPS was shown to be a novel technique for studying in-depth structural information of discrete cadmium layers in Langmuir-Blodgett multilayer films recently [116]. Here we report the structural modification in multilayer LB films after sulfidation using differential charging in angle-dependent XPS that are not observable by X-ray reflectivity technique. AFM study suggest less modification in compact LB films in comparison to the non-compact ones. The differential charging in the LB multilayers changes after sulfidation due to the formation of cadmium sulphide nanostructures in cadmium arachidate LB matrix which was reflected prominently in the differential charging of Cd3d5/2 XPS peaks. It was shown from chemical analysis by XPS that while internal structure was completely destroyed in initially non-compact cadmium arachidate LB films, in a compact film about 40% bilayer structure may remain intact after sulfidation. It was found that even after sulfidation the compact multilayer LB films were differentially charged in out-of-plane (in-depth) direction, whereas this kind of differential charging was not apparent in rough and non-compact films. Our results clearly indicate that for LB films with compact structure a partial layered structure survives the impact of particle formation, whereas for non-compact films the modification is large and no specific conclusion could be drawn. However, X-ray reflectivity data in that study was inconclusive about the presence of a layered
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structure. To further examine the validity of our prediction, in this section we have applied our differential charging analysis technique [116] to extract the information about the structural changes in the multilayer films induced by the formation of cadmium sulfide nanoclusters. Analyzing the differential charging obtained from angle-dependent XPS measurements in the sulfided samples we have shown that in initially compact LB films partial layered structure indeed survive after sulfidation as was proposed in our previous study.

4.3.2 Experimental

Langmuir–Blodgett film of different thickness with different structures have been prepared with the conventional LB deposition technique using a KSV 5000 instrument as discussed in the earlier section. We have prepared three 5-ML LB film at surface pressure 30mN/m, 20mN/m, and 40mN/m and were referred to as sample A, B, and C respectively. It was observed that the films grown at 30mN/m (sample A) were compact whereas those grown at 20mN/m (sample B) and 40mN/m (sample C) were rough and non-compact in nature as discussed in previous section. A 3-ML was also prepared at 30mN/m. All the films were exposed to \( H_2S \) gas (BOC, UK, 99.5%) in a closed glass tube for 15 min, as this time was sufficient for completeness for sulfidation reaction [114], to produce cadmium sulphide (\( CdS \)) nano particles in LB matrix.

XPS measurements were performed with an Omicron Multiprobe (Omicron NanoTechnology, UK) spectrometer fitted with an EA125 hemispherical analyzer and a monochromatized \( AlK\alpha \) (1486.6 eV) source. All data were collected at pass energy 40 eV with analyzer angular acceptance ±1°. The background correction of the data was done by Shirley method [169]. The curve fitting of the core XPS lines was carried out using Gaussian–Lorentzian sum (GL) functions. Surface topography of all the films was studied by AFM (NanoScope IV) in tapping mode. To measure the bilayer separation and the thickness of the films, X-ray reflectivity (XRR) measurements were performed using an X-ray diffractometer (D8 Discover, Bruker AXS) with \( CuK\alpha \) radiation (\( \lambda = 0.154 \) nm). The density distributions of the layered structure
of the LB films are determined by fitting the data to a model based on Parratt formalism [150].

### 4.3.3 Results and Discussions

#### Structure and morphology

In the previous section, we have shown that CdS nanoparticles of around 4.5 nm are formed in the LB films with different compactness on sulfidation [114]. As a result of the internal pressure developed due to the particle formation and subsequent molecular movements in the non-compact films B and C there was a large change in the interior and the film surface as discussed previous section. On the other hand the surface morphology of the compact film was changed only slightly through filling of the surface pores. Figure 4.3.1 shows the AFM topographic images for compact samples A before and after sulfidation. It is shown in the figure that uniform film with distributed pinhole defects at the surface was deposited for sample A. Although the surface topography appears to be different after sulfidation, the analysis reveals that mainly the defects (empty space) are filled in due to lateral expansion of the film as shown in the figure. RMS roughness values for the images before and after sulfidation were nearly the same.

In addition to the study of in-plane morphological evolution by AFM, X-ray reflectivity studies were performed to understand the out-of-plane structures and the interfacial properties of all the films prepared at different conditions before and after sulfidation. Out-of-plane structure of the non-compact films were largely modified after sulfidation as there was large free space available for molecular movements [114], whereas, for the compact film the change was less as indicated by the AFM data discussed above. The reflectivity data (open circles) with fitted lines and the corresponding electron density profiles ($\rho$) for sample A before and after sulfidation are shown in figure 4.3.2. Electron density profile shows (inset, figure 4.3.2) presence of discrete cadmium layers in the multilayer structure for sample A before sulfidation as expected. After reaction with $H_2S$ the film structure was modified and the electron
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Figure 4.3.1: AFM images of 5-ML LB film (sample A) of cadmium arachidate on silicon substrate. Inset shows the image of the same film after sulfidation.

density was found to decrease continuously from the first layer with presence of some irregular higher density regions. It may be noted that these higher density regions could appear due to the presence of cadmium head groups in forms of ion or particles in the film. However, as this method provides an average information over the probe size, the existence of the high density cadmium head groups for any surviving domains could not be estimated correctly from the present XRR results.

XPS study: application of differential charging technique

Normal take-off angle XPS

The recently developed [116] differential charging analysis technique was found to be dependent only on the difference between the charging conditions of the individual vertically separated layers. If there are surviving layered regions after sulfidation of the films, the vertical differential charging in these films are likely to occur. Hence the effect should be observed in terms of change of peak shape in angle-dependent
XPS measurements. However, as the peak shifting/broadening in XPS may also occur due to chemical shift, it is important to first understand if they are due to the presence of different chemical environments or due to charging. This can be done by noting the behaviour of the data with respect to some kind of neutralisation of the surface. Here we have used biasing induced charging/neutralisation technique for this purpose. XPS data of all the samples were taken at various negative and positive sample bias conditions. If there is any differential charging, it can be increased (decreased) by the application of negative (positive) bias by repulsion (attraction) of stray electrons available in the chamber. Figure 4.3.3a shows $\text{Cd}^{3d_{5/2}}$ XPS lines at different sample bias for sample A as a typical case. It can be observed from the figure that the peak shape approaches towards a single peak as the bias voltage is increased to +30V. This is due to neutralization via attraction of stray electrons by the positively biased sample. The detailed variation of binding energy difference (between the differentially charged peaks, $\delta V$, fitting not shown) with sample bias for sample A and B are shown in figure 4.3.3b. Both samples show similar sigmoidal variation with change of bias, however, the magnitude of charging was higher in
4.3. Application of differential charging characterization method to the modified LB films

Figure 4.3.3: (a) Cd3d5/2 core level XPS lines for sample A measured with the application of dc electrical bias to the sample. Three typical cases for -30V, 0V and +30V are shown as indicated. (b) Binding energy difference ($\delta V$) vs. the bias voltage of Cd3d5/2 lines for the sample A and B. The fitted lines are given as guide to eyes.

The changes in binding energy difference $\delta V$ with bias voltage for all the samples indicate that differential charging and not the chemical shift was responsible for the splitting or widening of the peaks.

Cd3d5/2 and Cls core level spectra for all the samples are collected at normal take-off angle. The line shape for the as grown three films were different as shown in figure 4.3.4. Panel I of figure 4.3.4 clearly shows that Cd3d5/2 XPS spectra for the samples are broad and fitting requires at least two GL functions. We have discussed above that this peak broadening was due to the differential sample charging. Cls XPS spectra for the LB films are shown in panel II of figure 4.3.4. There are two peaks in the Cls spectra for all the films, a strong peak at lower binding energy corresponding to $CH_2$ and $CH_3$ carbon atoms and a very weak peak at higher binding energy (around 290.0 eV) corresponding to the carboxyl carbon atoms of the arachidate chains. As the intensity of the higher binding energy peak is very low, the detailed analysis of that peak was not performed (peak positions are given in table 4.3.1). The intense Cls peak at lower binding energy was also required to be fitted with two components due to differential charging. The positions and relative intensities of the deconvoluted components for Cd3d5/2 and Cls peaks are shown in...
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Figure 4.3.4: Normal take-off $\text{Cd}3\text{d}_{5/2}$ and $\text{C}1\text{s}$ core level XPS lines for as grown three samples. Panel I and II describe the $\text{Cd}3\text{d}_{5/2}$ and $\text{C}1\text{s}$ core level lines respectively. Sample descriptions are indicated in figure.

table 4.3.1. Binding energy positions and the relative intensities of these components are different for all the multilayer LB films prepared at different surface pressures.

XPS study has also been performed for all the LB films after reaction with hydrogen sulphide gas. It was shown that after reaction $\text{CdS}$ nanoparticles are formed in the LB matrix [114]. Similar to the unreacted samples $\text{Cd}3\text{d}_{5/2}$ and $\text{C}1\text{s}$ peaks are fitted with two components as they do not fit well with a single peak. The positions of the peaks for all the samples are found to be lower with respect to that of the unreacted samples as shown in table 4.3.1. This may be due to lower charging of the films as a result of lowering of film thickness after sulfidation [114].
Table 4.3.1: Position and relative intensity of two fitted components of Cd3d$_{5/2}$ and C1s spectra for all the samples (sample A, B, and C). The last column shows the binding energy (BE) of the carboxyl carbon.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Position of low BE peak (eV)</th>
<th>Position of high BE peak (eV)</th>
<th>Relative intensity of low BE peak (%)</th>
<th>Relative intensity of high BE peak (%)</th>
<th>BE of carboxyl carbon (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cd3d$_{5/2}$</td>
<td>C1s</td>
<td>Cd3d$_{5/2}$</td>
<td>C1s</td>
<td>Cd3d$_{5/2}$</td>
</tr>
<tr>
<td>A</td>
<td>405.8</td>
<td>285.5</td>
<td>407.3</td>
<td>286.7</td>
<td>23.0</td>
</tr>
<tr>
<td>B</td>
<td>406.3</td>
<td>285.5</td>
<td>407.6</td>
<td>286.8</td>
<td>13.4</td>
</tr>
<tr>
<td>C</td>
<td>406.1</td>
<td>285.5</td>
<td>407.5</td>
<td>286.8</td>
<td>10.8</td>
</tr>
<tr>
<td>A(H$_2$S)#</td>
<td>405.8</td>
<td>285.1</td>
<td>406.6</td>
<td>286.0</td>
<td>38.2</td>
</tr>
<tr>
<td>B(H$_2$S)#</td>
<td>405.7</td>
<td>285.3</td>
<td>406.5</td>
<td>286.4</td>
<td>90.0</td>
</tr>
<tr>
<td>C(H$_2$S)#</td>
<td>405.9</td>
<td>285.5</td>
<td>406.3</td>
<td>286.7</td>
<td>94.3</td>
</tr>
</tbody>
</table>

$^a$A(H$_2$S), B(H$_2$S) and C(H$_2$S), referred to the sample A, B and C after sulfidation.
Angle-dependent XPS

As we have observed earlier [116] that differential charging was more prominent for the discrete cadmium layers as compared to the continuous carbon stacks in LB films, $Cd3d_{5/2}$ core level spectra were measured at different take-off angles ($90^\circ$ to $30^\circ$) for all the samples here. Figure 4.3.5 shows the $Cd3d_{5/2}$ lines at three different angles for sample A (before and after sulfidation) and B (sample C is similar to sample B, not shown). For sample A the peak gradually splits to two distinct peaks at grazing angles and peak deconvolution requires two GL functions to fit the data for all angles as shown in figure 4.3.5a. The intensity of the lower binding energy peak was found to increase at grazing angles. The reduction of photoelectron signal as a function of depth ($z$) and take-off angle ($\theta$) can be expressed as

$$A(z, \theta) = \exp \left( -z \frac{\lambda}{\lambda \sin \theta} \right)$$

where $\lambda$ is the inelastic mean free path of a particular species in the film. Once the possibility of chemical shift is eliminated the above results indicate that there is an in-depth potential gradient in the sample which broadens/splits the peaks at grazing angles. The interesting fact is that there are always some unavoidable stray electrons in a vacuum chamber fitted with ion gauge, X-ray source etc. and the partial neutralization of the sample due to these electrons causes the vertical differential charging if there is a layered structure in the system.

In figure 4.3.5b we have shown the data for sample A after sulfidation at different take-off angles. At a first glance the data for three different angles looks similar in absence of any prominent feature to differentiate between them. However, fitting with single peak was not possible for the whole set of data. Taking the clue from the pre-sulfidation data, we attempted a similar fitting procedure considering the fact that layered structures were largely damaged in this film due to sulfidation. It was interesting to note that similar angle-dependent charging related features with reduced peak separation was present for sample A after reaction with hydrogen sulphide gas. In this case the peaks were only asymmetric and broadened as the
Figure 4.3.5: XPS $Cd3d_{3/2}$ core level lines measured for (a) sample A, (b) sample A after sulfidation and (c) Sample B at different take-off angles.
magnitude of differential charging was less here. This may be explained in terms of two facts. Firstly, the layered structure that survives after \( \text{CdS} \) formation, loses the uniformity and also may lower the interlayer separation (separation between charged peaks is proportional to inter layer spacing), secondly the additional cadmium signal that comes from the dispersed \( \text{CdS} \) particles may lead to the broadening of the differentially charged peaks.

Although for samples B and C also two peaks were required to fit the \( \text{Cd}3d_{5/2} \) data as shown in figure 4.3.5c, the angular dependence of these data was not very apparent here. This indicates that even if there are layered structures the systematic behaviour in the angular dependence of the data does not sustain due to the large amount of defects in these films.

**Structural information from differential charging**

Analysis of in-depth differential charging has been used here for the determination of structural aspects of the multilayer LB films before and after sulfidation. The technique has been used only for sample A where in-depth differential charging was prominent. In-depth differential charging in multilayer LB films create a situation such that upper part of the film is relatively neutral with respect to the lower part. Assuming two embedded homogeneous cadmium layers at depth \( d_1 \) and \( d_2 \) with two different charging conditions (in-depth differential charging) in the LB films, the ratio of intensities of the photoelectrons emitted from the upper layer to that of the lower can be expressed by equation 4.1.5 as discussed earlier [116, 206].

In figure 4.3.6a and 4.3.6b we have plotted intensity ratio of lower binding energy (upper layer) to that of higher binding energy (lower layer) peaks of differentially charged \( \text{Cd}3d_{5/2} \) lines obtained from angle-dependent XPS measurements for sample A (5–ML LB film as shown in figure 4.3.5) before and after sulfidation. The intensity ratios were fitted using equation 4.1.5 as shown in figure 4.3.6a and 4.3.6b and the fitted results are shown in table 4.3.2.

It is important to note that the values of \( d \) in the expression of \( d_{\text{eff}} \) obtained from the fitting, represent the gap between the neutral cadmium layer close to the
Figure 4.3.6: Intensity ratio of lower to higher binding energy peaks of Cd$^{3d_{5/2}}$ for (a,b) 5-ML and (c,d) 3-ML LB films of cadmium arachidate before and after sulfidation as functions of take-off angles. Circles represent data and the solid lines are the fittings using equation 4.1.5.

Table 4.3.2: Comparison of different parameters obtained for the multilayer LB films. $d_{\text{model}}$: separation between the two differentially charged cadmium layers calculated from XRR results according to our model (see text for detail), $d$: obtained separation between the two differentially charged cadmium layers from angle-dependent XPS measurements using equation 4.1.5.

<table>
<thead>
<tr>
<th></th>
<th>5-ML LB film</th>
<th>3-ML LB film</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before sulfidation</td>
<td>After sulfidation</td>
</tr>
<tr>
<td>$d_{\text{model}}$ (Å)</td>
<td>76.3</td>
<td>-</td>
</tr>
<tr>
<td>$d$ (Å)</td>
<td>72.5</td>
<td>60.8</td>
</tr>
</tbody>
</table>
top surface and the average position of all other cadmium layers in the interior of the films as shown in the schematic (figure 4.3.7). The obtained value of $d$ for sample A closely matches with the calculated separation (from XRR) for 5-ML LB film before sulfidation as shown in table 4.3.2. This value is found to be lower for the LB film after reaction with $H_2S$ which indicates that the effective separation between the two charged layers reduces after sulfidation. This can be attributed to the change in structure of films produced by the formation of $CdS$ particles.

To check the consistency of the above results a 3-ML LB film of cadmium arachidate has also been examined before and after sulfidation. Intensity ratio and the corresponding fittings are shown in figure 4.3.6c and 4.3.6d. In this case also the interlayer separation was found to reduce after sulfidation similar to the case of 5-ML LB films. It is interesting to note that the existence of layered structure after sulfidation was observable in the in-depth differential charging of the multilayer LB films. This information together with the post–sulfidation XRR results clearly indicates partial survival of layered structure after particle formation in LB films as has been proposed in our earlier section [114].

It may be noted here that the magnitude of change in structure corresponding to about 60% sulfidation was very high due to large interfacial roughness produced by distortion of cadmium layers in the films. This leads to loss of reflected intensity in the specular direction in XRR measurements and therefore the structure after sulfidation of the films was not clearly understood by this technique. As in XRR
4.3. Application of differential charging characterization method to the modified LB films samples are assumed to be homogeneous layers over the probe size, the presence of both modified and unmodified regions may lead to misinterpretation of the data. It may be mentioned here that as opposed to XRR technique which assumes a single homogeneous electron density over the probe size for a layer, the differential charging in XPS is sensitive only to the inter layer separation between the differentially charged layers. This method here was found to be a useful tool to observe interlayer separation in a partially damaged layered system. Furthermore, as XPS is sensitive to the chemical nature of the material, the present technique is applicable to layered structures where the layers have similar electron density with the embedding matrix.

4.3.4 Conclusions

Differential charging in angle-dependent XPS measurements has been used to investigate the structural aspects in multilayer LB films of cadmium arachidate deposited on silicon substrate at different conditions before and after sulfidation. In this study XPS results were complemented with XRR and AFM studies to observe the differences in the structure and morphology in the light of differential charging in XPS. The changes in the differential charging was initially observed for the LB films deposited with structural differences introduced through variation in subphase pressure. For LB films prepared at 30mN/m, AFM measurement shows uniform surface with distributed defects and XRR results show presence of discrete cadmium layers embedded in the multilayer hydrocarbon stacks. Whereas rough and non-uniform morphologies were observed for the films grown at 20mN/m and 40mN/m subphase pressures. Compact multilayer LB films of cadmium arachidate were differentially charged in vertical direction whereas rough and non-compact LB films do not show measurable vertical differential charging.

Morphological changes of the surface after sulfidation was large for the non-compact films, however, for the compact films the sulfidation induced changes were relatively less. The XRR data of the post sulfidation films do not provide sufficient information regarding the internal structure as a result of large molecular
4.3. Application of differential charging characterization method to the modified LB films rearrangement in these films. It rather shows that the total thickness of the films reduces after sulfidation in all cases. For the determination of structural changes after sulfidation, analysis of in-depth differential charging with the help of angle-dependent XPS measurements has been performed. In the support of our predictions, our results clearly indicate that for LB films with compact initial structure a partial layered configuration with reduced interlayer separation survive the impact of particle formation. This method here was found to be a useful tool to observe interlayer separation in a partially damaged layered system. Furthermore, as XPS is sensitive to the chemical nature of the material, the present technique is applicable to layered structures where the layers have similar electron density with the embedding matrix.