

Formation of Ultrathin Semiconductor Films by CdS Nanostructure Aggregation

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Formation of ultrathin films of CdS nanostructures on solid substrate has been achieved by selective removal of the fatty acid matrix from Langmuir–Blodgett films of cadmium arachidate exposed to an atmosphere of hydrogen sulfide. By means of nanogravimetric assays it was possible to monitor the formation of CdS nanoparticles during the reaction and to reveal the presence of a film, nonsoluble in organic solvent, after treating the sample with chloroform. Changes in the film structure due to the formation of CdS particles were shown by X-ray study. Optical ellipsometry made it possible to measure the average thickness of the obtained film. Optical absorption spectra proved the presence of Q-state CdS particles before and after removing the fatty acid matrix and showed, moreover, an increase of the effective size of the particles from about 3 to about 4.4 nm. STM of the CdS residual film revealed, in turn, an interconnected structure formed by bumps of about 2–3 nm in diameter when the film was obtained from one cadmium arachidate bilayer and a similar structure with bumps of increased size (4–5 nm) in the case of a sample derived from 20 bilayers, indicating that a mechanism of particle aggregation is responsible for the semiconductor film formation. In the latter case, atomic resolution was achieved, revealing a CdS lattice.

Introduction

Cadmium sulfide nanostructures have been formed by means of different techniques and in different environments such as zeolites,¹ polymers,² solutions,^{3,4} glasses,⁵ Langmuir–Blodgett (LB) films of fatty acid salts (cadmium arachidate,⁶ cadmium stearate,⁷ mercury arachidate,⁸ etc.) by exposing samples to H₂S. Their properties have been characterized by several techniques such as optical absorption,⁶ X-ray diffraction,⁷ electron diffraction,^{6,7} and optical ellipsometry,⁶ showing typical sizes smaller than 5 nm causing quantum effects such as the shift of the optical absorption band onset, connected with the band gap shift. Moreover, monoelectron phenomena in the behavior of the voltage–current characteristics of single CdS particles formed in LB films of cadmium arachidate, as measured by scanning tunnelling microscopy (STM), have been recently reported.⁹

Despite the lack of exhaustive information on the CdS particle's real shape,⁶ the LB technique seems to be the most suitable to achieve structures close to ultrathin semiconductor films, because it provides highly anisotropic initial conditions.¹⁰ In the case of cadmium arachidate LB film, for instance, cadmium atoms are disposed in a plane between the polar head groups of the fatty acids,¹⁰ and this fact could induce the formation of disk-shaped islands instead of ball-shaped ones during the reaction with H₂S. The possibility of having films of such nanostructures, displaying quantum behaviors, is, therefore, both of basic and applied interest. In fact, they could be very useful when trying to make electronic chips based on monoelectron phenomena, and, generally speaking, they work toward speeding up the signal treatment. However, X-ray small angle diffraction⁷ showed that the formation of CdS particles inside LB films is not in itself sufficient to make structures similar to superlattices (e.g. semiconductor superlattices), because the result of the reaction with H₂S is the formation of CdS particles segregated outside zones of closely packed fatty acids domains and not the appearance of thin layers of CdS.

For the formation of pure CdS thin films it is useful to have the possibility of monitoring the reaction of CdS structure formation in LB films and to find ways for removing selectively the fatty acid matrix from the film. Toward the aim of selective removal of fatty acids, several approaches have been developed since the beginning of LB science,¹¹ and recently, different methods have been proposed for the formation of thin metal oxide layers starting from LB films.¹²

We, hereby, report the results of a study devoted to the formation of thin CdS films. Several different experimental techniques have been used to investigate cadmium arachidate LB films during and after the reaction with H₂S and after the removal of the fatty acid matrix. The reaction of formation of CdS particles has been real-time monitored by means of a nanogravimetric gauge¹³ which helps in estimating the mass amount (Δm) formed on the surface of a quartz resonator by measuring the shift (Δf) from its resonance frequency (f_0) according to the Sauerbrey equation:¹⁴

$$\frac{\Delta f}{f_0} = - \frac{\Delta m}{A \rho l} \quad (1)$$

where A is the area covered by the deposited layer, ρ is the quartz density, and l is the resonator thickness.

X-ray diffraction was used for studying the structural changes in the film due to the particle formation process. Moreover, optical ellipsometry was applied to show the variation of the film thickness after reaction with H₂S and subsequent removal of the fatty acid matrix. CdS nanoparticle formation and the effect of washing the sample with chloroform were proved by optical absorption spectra. STM helped in investigating the structure of the residual film.

Materials and Methods

Langmuir–Blodgett films of cadmium arachidate were formed in a commercial (MDT Co., Russia) trough,¹⁵ by spreading 40 μ L of 1 mg/mL chloroform solution of arachidic acid (Sigma Co.) on the surface of a water subphase (Milli-Q system, resistivity of 18.2 M Ω cm) containing 10⁻⁴ M CdCl₂

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(pH 6.8) and deposited on a solid substrate at 27–30 mN/m surface pressure by a vertical dipping technique (dipping speed was 0.2 mm/min).¹⁰

Different substrates were used for the various experimental assays, namely, quartz crystal cuts for nanogravimetric assays, silicon plates for X-ray study and ellipsometry, 1 mm thick quartz cuvettes for optical absorption, and freshly cleaved highly oriented pyrolytic graphite for STM investigation.

All the samples were exposed to H₂S atmosphere in order to achieve cadmium sulfide and protonated fatty acid.⁶

The reacted samples were washed by immersing them in chloroform three times for 1 min each time (using every time a new portion of chloroform) and dried with nitrogen flow.

Nanogravimetric assays were performed by means of a homemade gauge with a sensitivity of 0.57 ± 0.18 ng/Hz.¹³ Quartz resonators (10 MHz) with aluminium electrodes were used as mass transducing gauges. Before covering them with cadmium arachidate LB film, they were exposed to H₂S atmosphere in order to avoid any reaction on the surface of the electrodes during the experiments with cadmium arachidate samples. It was found that the surface of the resonators does not practically react with H₂S (frequency shift was on the order of magnitude of 10 Hz, corresponding to 5.7 ng).

The samples (20, 15, and 10 bilayers) were placed in a glass vessel closed and connected by a tube with the reactor where H₂S was forming. The tube was equipped with an apparatus to introduce the gas flow at the beginning of the experiments.

X-ray measurements ($\lambda = 0.154$ nm) were carried out with a small angle X-ray diffractometer with a linear position-sensitive detector providing an angular resolution of 0.02° .¹⁶

Ellipsometric measurements were carried out with a PCSA null ellipsometer using a He–Ne ($\lambda = 632.8$ nm) laser source. The data were processed according to the two-layer model.¹⁷

Spectrophotometric measurements were performed with a J-7800 (Jasco, Japan) spectrophotometer in the wavelength range 200–500 nm.⁶

STM (MDT Co., Russia)¹⁸ measurements were performed in constant current mode and in constant height mode (for high resolution) in the bias voltage range 0.1–0.5 V and tunnelling current range of 0.5–2 nA with Pt–Ir (90%–10%) mechanically cut tips. Samples were imaged twice, just after the preparation and after 2 days, displaying no significant differences.

Results and Discussion

Nanogravimetric tests were performed to provide an insight into the rate of formation of CdS particles in LB films of cadmium arachidate and to estimate the reaction yield upon the number of deposited bilayers. Figure 1 shows the increase in mass on the quartz surface as a function of the exposure time to H₂S atmosphere. The time for attaining the saturation level increases with the number of layers. On the other hand, the plateau level in all three cases matches rather well with the value resulting from simple calculations of the number of cadmium atoms available for the reaction in each sample,¹² Table 1. The available amount of cadmium atoms was estimated taking into account that one atom coordinates the head groups of two fatty acid molecules, and in the pH (6.5–6.8) range used in this work, the amount of salt in the film should be 70% (30% being the fraction of pure fatty acid molecules).¹⁹

The washing of the samples with chloroform and their drying in nitrogen flow result in the removal of a mass amount corresponding to the amount of fatty acids present on the resonator surface, Table 1. This procedure, however, did not remove completely the film from the quartz surface, leaving

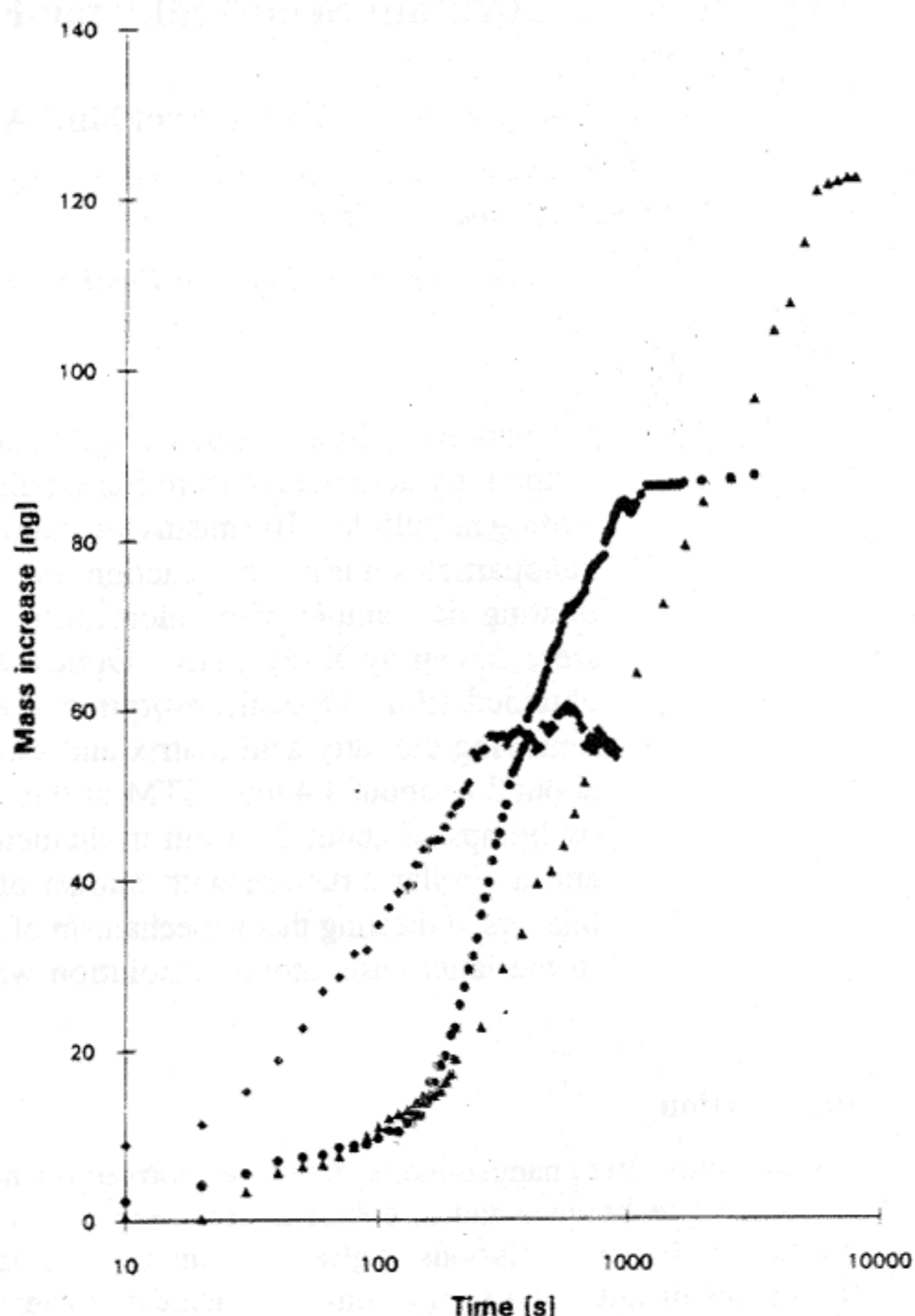


Figure 1. Real-time monitoring of the reaction between H₂S and cadmium arachidate in three different samples (20 bilayers, \blacktriangle ; 15 bilayers, \bullet ; 10 bilayers, \blacklozenge). Films were deposited onto both sides of the resonators.

TABLE 1: Nanogravimetric Assay Results^a

no. of bilayers	reacted H ₂ S (theory)	reacted H ₂ S (exptl)	fatty acid density (theory)	fatty acid density (exptl)	residual film (theory)	residual film (exptl)
20	3.86	3.4 ± 0.2	101.16	97 ± 5	14.3	12.4 ± 0.6
15	2.89	2.5 ± 0.1	75.87	72 ± 4	10.7	9.3 ± 0.5
10	1.93	1.6 ± 0.1	50.58	47.8 ± 2	7.1	6.5 ± 0.3

^a All values are expressed in nanograms per square millimeter. The experimental errors are due to the error in the determination of the proportionality coefficient between frequency shift and surface density.¹³ The theoretical amount of the residual film is calculated on the basis of the Cd atom number which derives from the amount of reacted H₂S (one Cd for one S). Close packing of the hydrocarbon chains is assumed for all the calculations.

the residual mass amount listed in Table 1. Taking into account both the amount of reacted H₂S and the mass of the residual film (nonsoluble in chloroform, contrary to hydrocarbon chains), it could be argued that the residual film is made of CdS structures which were formed during the reaction.

The X-ray study was carried out in order to understand the way in which the reaction affects the film structure during particle formation. The results of the diffraction study of 10-bilayer cadmium arachidate LB film just after deposition, after the reaction with H₂S, and after washing the reacted film with chloroform are reported in Figure 2. The X-ray pattern of nonreacted films contains a system of Bragg reflections corresponding to a spacing value of 5.45 ± 0.05 nm. The angular position of Kiessig fringes gives a film thickness of 55 ± 2 nm. After the reaction, the spacing value increased slightly (5.60 ± 0.05 nm) as well as the total thickness (59 ± 2 nm).

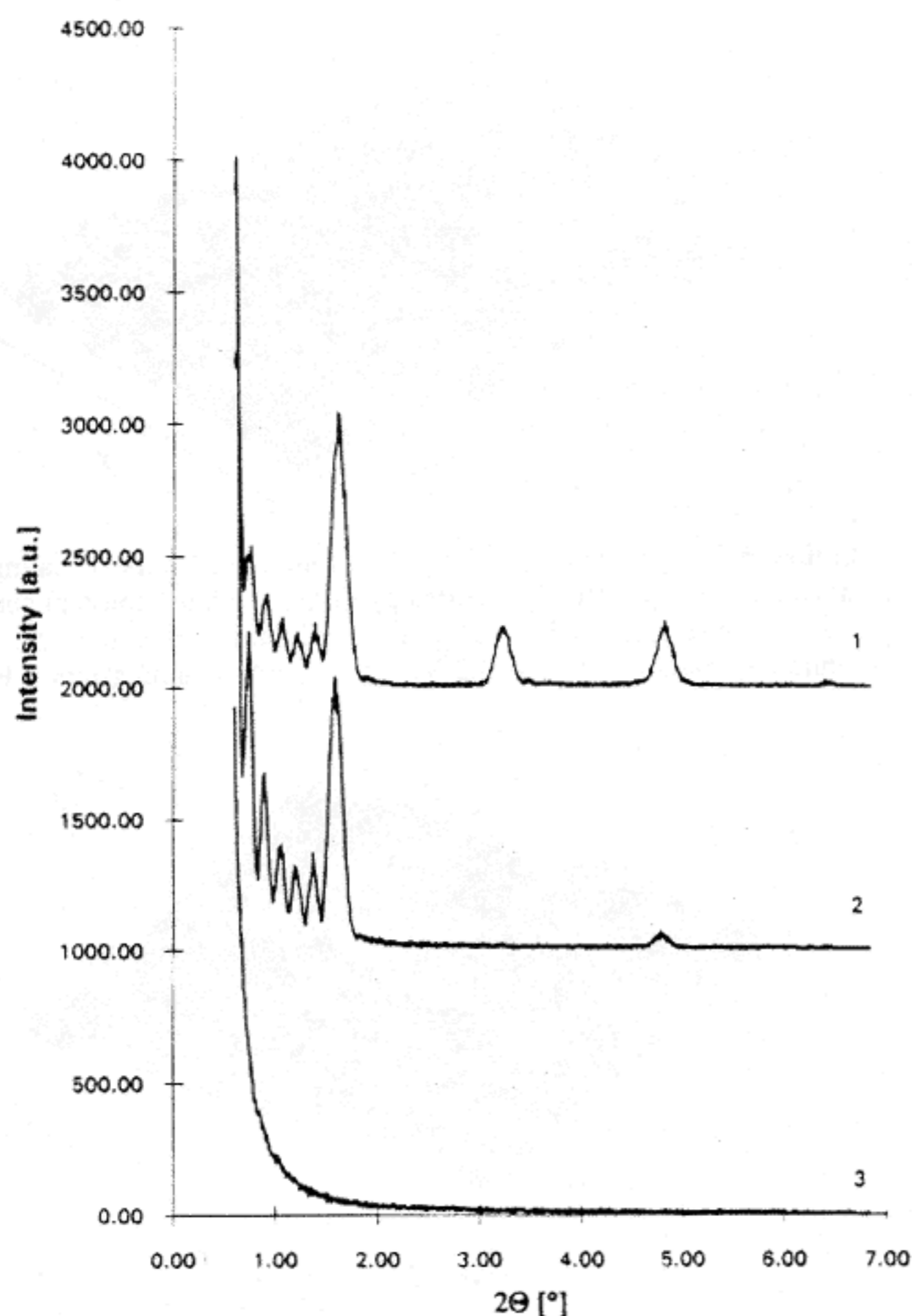


Figure 2. X-ray diffraction patterns of 10 bilayers of cadmium arachidate LB films just after deposition (1), after reaction with H_2S (2), and after washing them with chloroform (3).

Moreover, the even reflections disappeared completely from the pattern. All this evidence points out the removal of cadmium from the bilayer structure. In fact, the increase of the spacing can be explained by the substitution of Cd by two hydrogen atoms in the head groups. Even a simple consideration of the atomic and ionic radii of the elements gives about a 0.1 nm increase in the bilayer thickness. The disappearance of peaks means that the even harmonics make no contribution to the electron density profile, consistent with the marked decrease in the electron density in the middle of the bilayer (cadmium was replaced by two hydrogen atoms). These results are different from those previously obtained on lead stearate films⁷ exposed to H_2S when, after the reaction, an increased tilting of the hydrocarbon chains of the stearic acid was registered. The difference is likely due to the different procedure used for the treatment with H_2S (in the present case the reaction was carried out much more slowly).

After washing the sample with chloroform, no Bragg reflections were registered in the same angular range, implying that all the periodical structures due to hydrocarbon chain close packing have been removed.

Furthermore, optical ellipsometry was applied to estimate the thickness of the film at various stages of the sample preparation process, obtaining the results which are reported in Table 2. These results confirm the increased thickness of the film after the reaction with H_2S and prove the presence of a residual film after the removal of fatty acid molecules. This film has a thickness corresponding to the difference between that of the LB film before and after the reaction with H_2S . The small discrepancy between this difference and the CdS film thickness, which is however within the experimental error limits, can be

TABLE 2: Ellipsometric Assay Results^a

	before H_2S	after H_2S	after chloroform
film thickness per monolayer	2.7 ± 0.1	3.3 ± 0.1	0.4 ± 0.1

^a All values are expressed in nanometers. The results were obtained by analyzing films with a different number of layers and averaging the data.

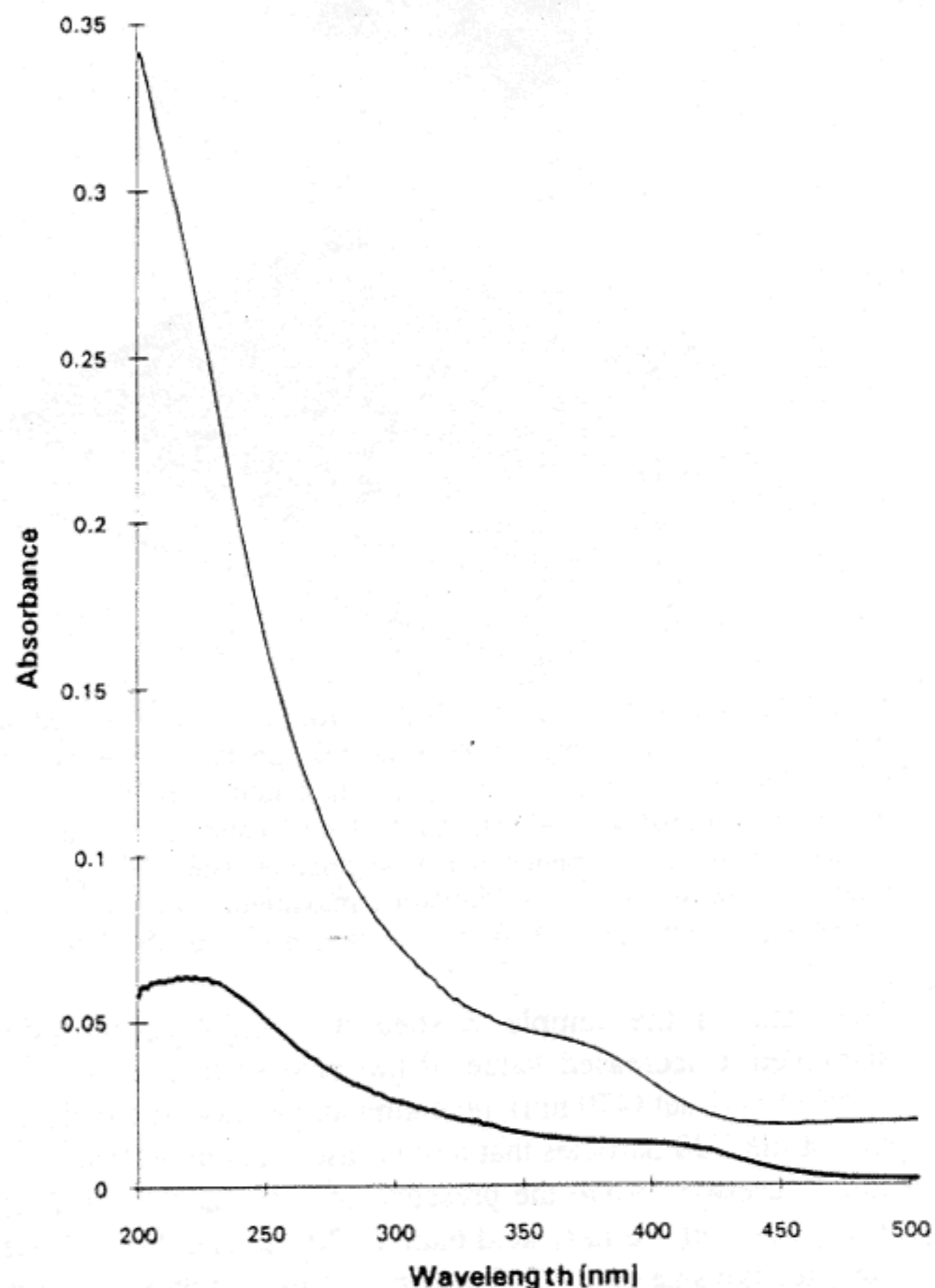


Figure 3. Optical absorption spectra of 20 bilayers of cadmium arachidate LB film after reaction with H_2S (thin line) and after washing with chloroform (thick line).

accounted for by the marked difference in the values of the refraction index. Besides, the data on the reacted film thickness are in agreement with those obtained from the angular position of the Kiessig fringes in the X-ray experiment. By measuring the refraction index of the residual film and assuming that it is the effective value of a mixture of CdS and air (porous film), a film density of $1.6 \pm 0.3 \text{ g/cm}^3$ resulted, which is similar to that measured with the nanogravimetric probe ($0.77 \pm 0.29 \text{ g/cm}^3$), but different from the bulk value (4.82 g/cm^3). The difference is probably due to the poor homogeneity of the film.

Optical absorption measurements can provide a deeper insight into the properties of the formed particles, confirming that we are really dealing with CdS nanoparticles.^{6,20} Optical absorption measurements were performed on the reacted sample before and after washing it with chloroform. In Figure 3 the corresponding spectra are reported. The spectrum before washing shows, as expected, a blue shift (85 nm) in the absorption onset of CdS (435 nm) with respect to the bulk value (520 nm⁶) which is due to the quantum nature of the formed CdS particles. The observed blue shift is connected to quantum confinement effects. The empirical pseudopotential method implemented by M. V. Rama Krishna and R. A. Friesner²⁰ allows the estimation of the cluster sizes from the values of these shifts. They indicate a particle size of about 3 nm in the sample before washing.

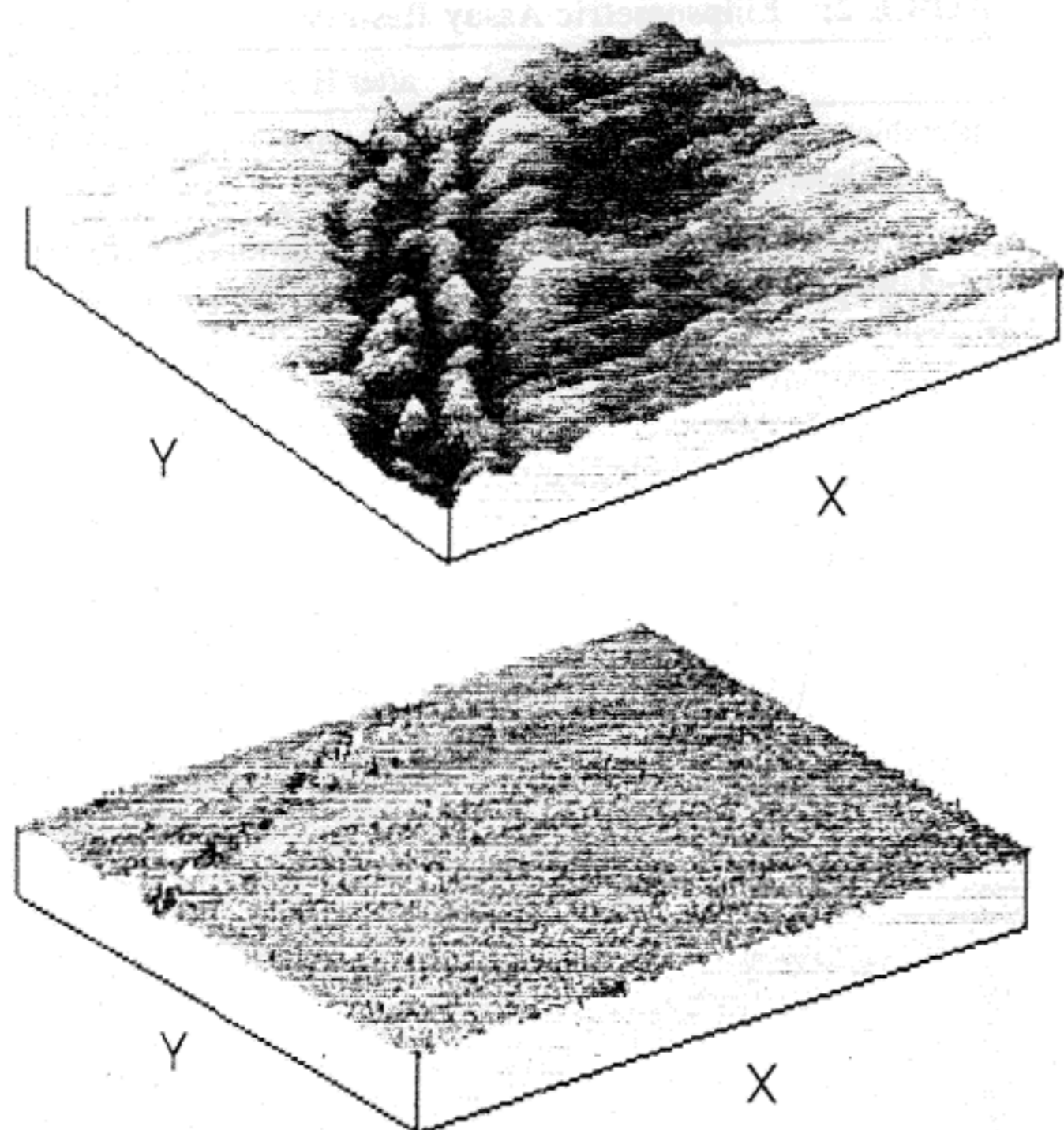


Figure 4. (a) STM image of CdS film from one bilayer of cadmium arachidate on top of highly oriented pyrolytic graphite: constant current mode; image size $25.6 \times 25.6 \text{ nm}^2$; maximum corrugation 1 nm; tunnelling parameters $V_t = 0.1 \text{ V}$, $I_t = 1 \text{ nA}$; scanning rate 12 Hz. (b) STM image of highly oriented pyrolytic graphite plate: constant current mode; image size $25.6 \times 25.6 \text{ nm}^2$; maximum corrugation 1 nm; tunnelling parameters $V_t = 0.15 \text{ V}$, $I_t = 1 \text{ nA}$; scanning rate 12 Hz.

The data on the sample washed with chloroform, instead, displayed a decreased value of the blue shift (50 nm) of the absorption onset (470 nm), revealing an increase in the effective size of the CdS particles that in this case is about 4.4 nm. These data, therefore, prove the presence of CdS particles also after the removal of the fatty acid matrix. Moreover, the increase in the effective size of the CdS structures upon washing the sample points out that there is a phenomenon of interconnection of the particles in the layer, which explains the fact that the layer is not removed together with the fatty acid molecules.

STM imaging was carried out in order to achieve a more direct insight into the structure of the residual CdS film. In the first attempt, only a bilayer of cadmium arachidate was deposited onto a plate of freshly cleaved highly oriented pyrolytic graphite, which, after the reaction with H_2S , was washed in chloroform. Figure 4a shows a typical view of a rather wide area of the sample surface. As is evident, a marked corrugation throughout the image is present, and mutually connected bumps, with an average size of 2–2.5 nm, are visible. The groove which crosses the image is very likely connected with a graphite step, and along it bumps are more evident. The comparison with an image of highly oriented pyrolytic graphite in the same scale (Figure 4b) underlines the difference in corrugation. The roughness should be due to CdS particles aggregated on the surface. Particle size estimated by the shift of the optical absorption band onset is in good agreement with that measured by STM. STM measurements on a thicker sample (obtained from 20 bilayers of cadmium arachidate) show once more a structure formed by interconnected, larger bumps, 4–5 nm in size, Figure 5. In this case, being possible to image the surface in the same tunnelling parameter range as that used for the monolayer (see captions to Figures 4 and 5 for comparison), it is also possible to argue that the aggregated film has good interconnections between the various particles which have been formed in different bilayers of the original arachidate film.

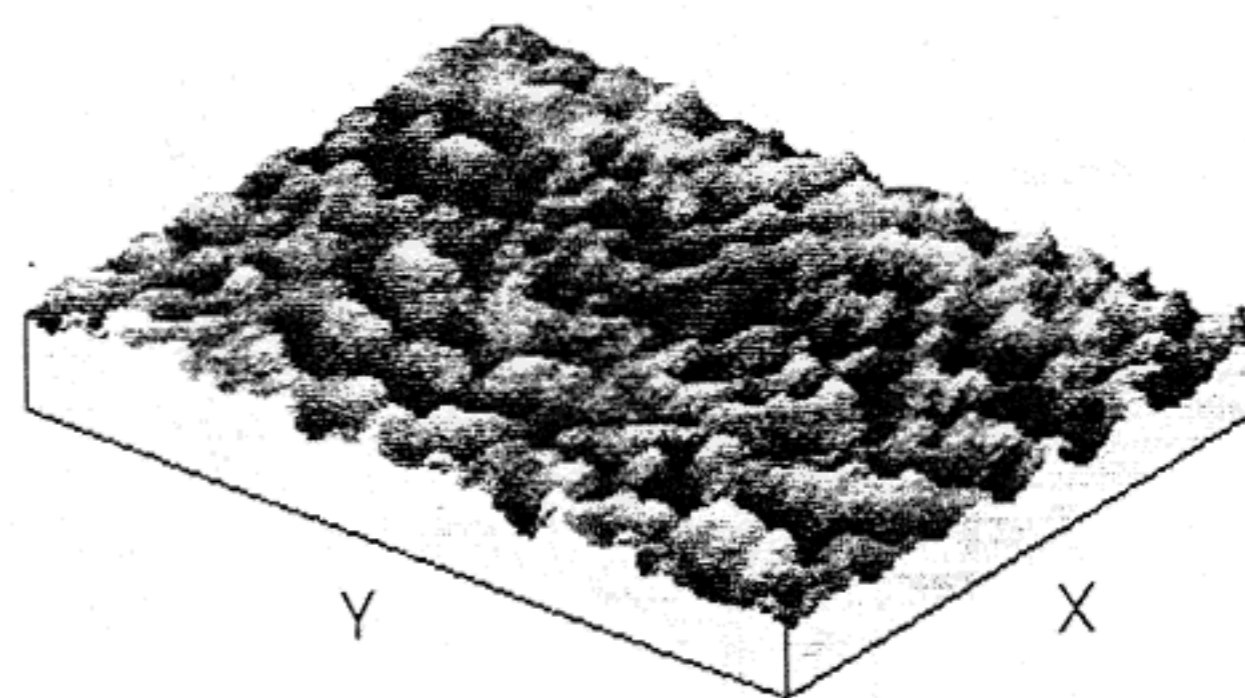


Figure 5. STM image of CdS film from 20 bilayers of cadmium arachidate on top of highly oriented pyrolytic graphite: constant current mode; image size $48.5 \times 64 \text{ nm}^2$; maximum corrugation 2.5 nm; tunnelling parameters $V_t = 0.2 \text{ V}$, $I_t = 1.2 \text{ nA}$; scanning rate 9 Hz.

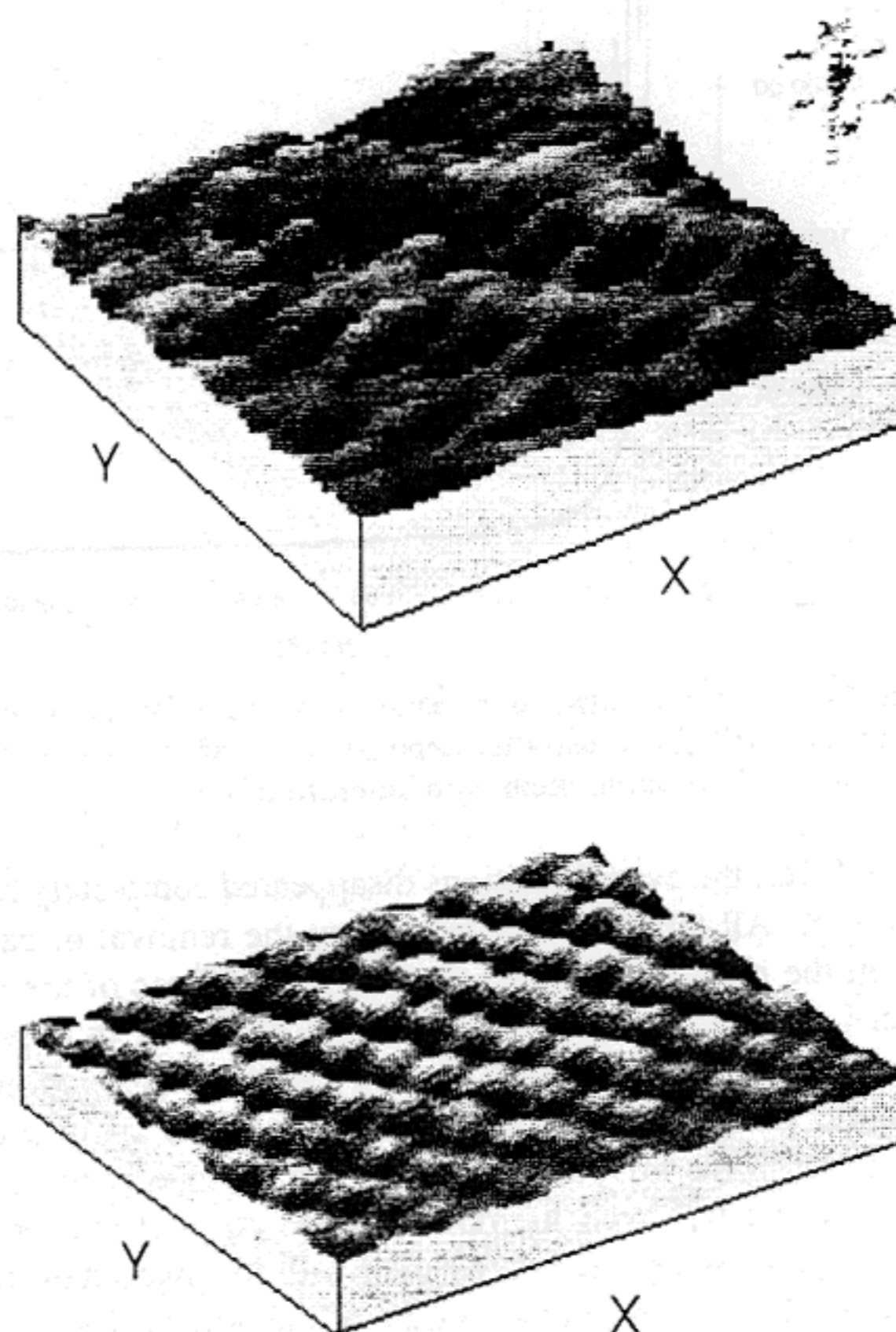


Figure 6. (a) STM image of CdS film from 20 bilayers of cadmium arachidate on top of highly oriented pyrolytic graphite: constant height mode; image size $2.1 \times 2.5 \text{ nm}^2$; current corrugation 0.5 nA; tunnelling parameters $V_t = 0.2 \text{ V}$, $I_t = 1 \text{ nA}$; scanning rate 25 Hz. The inset shows the Fourier spectrum of the lattice. (b) Highly oriented pyrolytic graphite lattice: constant height mode; image size $2.0 \times 1.9 \text{ nm}^2$; current corrugation 1 nA; tunnelling parameters $V_t = 0.1 \text{ V}$, $I_t = 1.5 \text{ nA}$; scanning rate 25 Hz.

Previously reported data⁶ have shown the independence of the average particle size upon the number of cadmium arachidate layers. Nevertheless, this fact does not contradict our results, as our samples also underwent the washing procedure with chloroform. This action, which is the cause of particle aggregation, can be responsible for the decrease in the particle size of the sample from one cadmium arachidate bilayer, as well.

In Figure 5 it is also possible to see flat regions, which could be suitable for obtaining high resolution. Figure 6a displays the results of high-resolution scanning of such a flat zone, performed in constant height mode, showing the CdS hexagonal lattice (see Fourier transform in the inset) with a period of 0.42

nm in comparison with the bare graphite lattice (0.246 nm), Figure 6b. As expected, the CdS lattice not only differs from graphite in the unit cell parameters but also shows more defects due to small monocrystal sizes and the crystal growing process.

Conclusion

Summarizing, the results show the possibility of formation of thin CdS films on solid substrates by washing with chloroform the film of cadmium arachidate which underwent H₂S treatment. The process of CdS particle formation in LB film was directly monitored by nanogravimetric assay. From the combined results of X-ray, ellipsometry, optical absorption, and STM studies it was possible to draw conclusions about the structure of the CdS film, made of closely interconnected particles, and about the process of its formation, which results from particle aggregation caused by the washing treatment.

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