

# Direct Evidence for an Ion-by-Ion Deposition Mechanism in Solution Growth of CdS Thin Films

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A systematic investigation of the mechanism of cadmium sulfide solution growth using atomic force and scanning electron microscopy was performed. The process that was studied involved the slow generation of sulfide ions via the controlled hydrolysis of thiourea in the presence of cadmium nitrate and triethanolamine, a chelating ligand. The formation of two types of films was observed, a mirrorlike primary film and a secondary layer of larger particles that was loosely attached to the first film. The substrates used for the deposition were either bare mica or mica with a partial self-assembled monolayer of octadecylphosphonic acid,  $\text{CH}_3(\text{CH}_2)_{17}\text{PO}_3\text{H}$ , which served as an internal height standard due to the formation of submonolayer islands  $18 \pm 2 \text{ \AA}$  tall. Islands of CdS were observed to nucleate on the remaining bare patches of mica suggesting a potential route to lateral surface patterning. The CdS grew to a height of 22–23 nm, leveled off by 6.5 h, and then proceeded to grow in scattered domains 60–70 nm tall with a few spots as high as 80–100 nm after 10 h. The mechanism of growth has been attributed to either involve attachment of colloidal particles to the surface or an ion-by-ion deposition process. Atomic force microscopy has provided compelling evidence that the latter mechanism is the correct one.

## Introduction

Sensitive photoconductors such as CdS and (Cd/Zn)S are useful for the room-temperature detection of visible and infrared radiation.<sup>1</sup> In addition, these semiconductors are crucial to the development of photochemical and photovoltaic cells. One of the most promising photocell designs uses thin films of photosensitizers interfaced with a window material such as cadmium sulfide in which the crystal lattice parameters of the two films are matched as coherently as possible.<sup>2–4</sup> A variety of photosensitizers have been proposed in order to achieve this match including  $\text{Cu}(\text{In,Ga})\text{Se}_2$ ,  $\text{CuIn}(\text{S,Se})_2$ ,  $\text{Cu}_2\text{S}$ , and  $\text{CuInSe}_2$ .<sup>5–7</sup> While  $\text{CuInSe}_2$  is strongly favored for photocell applications, photoelectric efficiencies of 16–17% have been reported for the two quaternary chalcopyrite semiconductors. Furthermore, the latter materials have an excellent lattice match between their (112) planes and the (001) wurtzite plane of (Cd,Zn)S solid solutions, and photocells constructed from them

show little absorption loss.<sup>5</sup> Although there are problems with the degradation of these materials and the migration of copper into the junctures between the two layers, much success has been achieved with tandem solar cells constructed in this manner.

Thin films of group 12 sulfides are usually obtained by sputtering, vacuum evaporation, spray pyrolysis, and chemical vapor deposition.<sup>8–11</sup> The development of methods for thin film solution growth of these sulfides could reduce manufacturing costs, allow greater flexibility in choice of substrate, and increase the economic feasibility of solar energy conversion. In particular, the direct deposition of both the sensitizer and window materials onto lightweight substrates from aqueous solution would be very attractive.

Studies of the solution growth of CdS began as early as 1961 at which time Mokrushin and Tkachev<sup>12</sup> reported two types of films formed on glass slides suspended in alkaline solutions of a cadmium acetate/thiourea mixture. These consisted of a primary layer of small colloidal particles that formed a compact mirrorlike film and a secondary layer of larger particles

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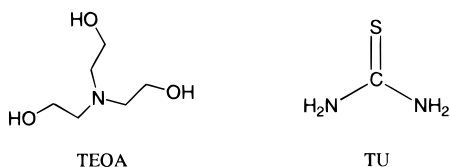
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that loosely attached to the first layer. Since this initial report, experimenters have modified the film growth by adding complexing agents, adjusting pH, bath temperatures, and deposition times, and changing the cadmium and sulfide-releasing reagents (e.g., thiourea or thioacetamide).

Specific reaction conditions for solution growth profoundly affect the resulting film morphology and composition. The solution pH influences not only the rate of thiourea or thioacetamide hydrolysis but also the variety of cadmium species present in the reaction mixture (such as  $\text{Cd}(\text{OH})_2$  and  $[\text{Cd}(\text{NH}_3)_4]^{2+}$ ).<sup>13</sup> Additionally, complexation of cadmium by agents such as chloride and triethanolamine (TEOA) modifies the growth rate and quality of the generated films.<sup>14</sup>

It has been suggested<sup>15</sup> that the primary layer observed during solution growth of cadmium sulfide is formed by an "ion-by-ion" deposition of  $\text{Cd}^{2+}$  and  $\text{S}^{2-}$  onto the substrate surface. The subsequent growth of the secondary layer then occurs as colloidal CdS particles, which are generated in solution, adsorb onto the substrate. Evidence cited to support the atomistic, ion-by-ion growth model included the film's strong adhesion, its high specular reflectance, and the fact that epitaxial growth was observed in the solution growth of  $\text{Pb}_{1-x}\text{Hg}_x\text{S}$  under similar conditions.<sup>16</sup> The same study used electron diffraction to determine that the primary films were composed of either pure hexagonal or a mixture of hexagonal and cubic phases of cadmium sulfide. Results for this experiment showed that stirring increased the prevalence of hexagonal crystals in the primary layer. This contrasts reports by other authors that 0.8–1  $\mu\text{m}$  thick CdS films grown at 80–90 °C on a spinning glass substrate, using a cadmium sulfate and thiourea solution in ammonium hydroxide, were found to be composed of 90% cubic and 10% hexagonal phases by both electron and X-ray powder diffraction (XRD).<sup>17</sup> Clearly, crystal type is highly dependent on experimental conditions.



Recently, Sebastian et al.<sup>18</sup> optically characterized a variety of film morphologies observed for a range of reaction conditions in alkaline solutions. Films were grown on glass at different ratios of  $\text{Cd}(\text{NO}_3)_2$ ,  $\text{NH}_4\text{OH}$ , triethanolamine (TEOA), and thiourea (TU). It was reported that films prepared under conditions of relatively high TEOA concentration, high pH, and low TU concentration displayed the least diffuse reflectance,

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suggesting that a uniform film with particles of small crystallite size had formed. Additionally, both cubic and hexagonal crystals of CdS were detected in the films by X-ray powder diffraction (XRD).

Herein, we report the results of an investigation of the growth of cadmium sulfide thin films on mica using conditions similar to those reported by Sebastian et al.<sup>18</sup> To more clearly distinguish the properties of the primary thin film from that of the secondary layer, sonication was used to remove the adsorbed particulate layer from the mica substrate. The more strongly attached primary layer was then characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The resolution of the latter instrument in the Z-axis is usually within an angstrom, but it varies, depending on the height of features and surface roughness. Therefore, it was possible to examine the very early stages of film growth using AFM. Thus, a more definitive characterization of the mechanism of solution growth of cadmium sulfide was achieved than was previously reported.

## Experimental Section

Triethanolamine (Aldrich),  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (Fisher), thiourea (Baker), and concentrated ammonium hydroxide (Chem-pure) were commercial reagents (ACS grade or better) and were used without further purification. All solutions were prepared using water from a Millipore Mill-Q system.

Metal and sulfur contents of cadmium sulfide films and precipitates were determined by inductively coupled plasma atomic-emission spectroscopy (ICP-AES) on a Perkin-Elmer Optima instrument or by X-ray fluorescence (XRF) spectroscopy on a Spectro X-Lab energy-dispersive XRF spectrometer. X-ray powder diffraction patterns were obtained using  $\text{Cu K}\alpha$  radiation on a Scintag XDS 2000 diffractometer equipped with an automated sample changer and a high-resolution solid-state detector. Jade, a search/match software package, was used in the identification of XRD spectra. UV/visible spectra were obtained using a Hewlett-Packard 8452A diode array spectrophotometer. Atomic force microscopy was performed on a Digital Instruments Nanoscope III AFM instrument, while scanning electron micrographs were obtained on a JEOL JSM-820 scanning electron microscope. Elemental analysis of the CdS films was performed on an AMRAY 1700 Turbo SEM equipped with a Tracor Northern EDXRF, energy-dispersive fluorescent X-ray detector. The cadmium sulfide films were also characterized by their sulfur  $L_{2,3}$  soft X-ray emission spectra on Beamline 8<sup>19</sup> at the Advanced Light Source using a previously published method.<sup>20</sup>

**Growth of CdS on Mica.** The solution growth of cadmium sulfide was performed using a similar approach as that utilized by Sebastian et al. to prepare films on glass.<sup>18</sup> The chemical baths were prepared by combining aqueous solutions of triethanolamine (30 mL of a 0.20 M solution, 6.0 mmol),  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (2 mL of a 0.10 M solution, 0.20 mmol), and thiourea (2 mL of a 0.20 M, 0.40 mmol) and concentrated  $\text{NH}_4\text{OH}$  solution (0.14 g, 1.12 mmol) within 3 × 3 × 8 cm TLC developing chambers. Sheets of ruby, muscovite mica (S & J Trading, Inc.) were cut to the size of approximately 2 × 4 cm and were peeled apart with a razor blade, to expose fresh faces of mica layers. The strips of mica were placed vertically in the chemical baths so that the ridges on the inside of the chamber held the strips upright and kept them from touching one another.

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Time-elapsing growth was observed by placing five strips of mica in a reaction solution and then removing a strip at 3, 5, 7, 9 and 12 min. The strips were rinsed and sonicated for 5 min in Millipore water and were then air-dried overnight before being examined by AFM.

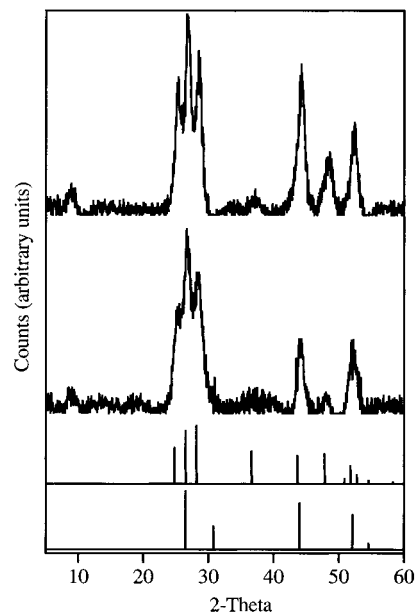
During the solution growth of the cadmium sulfide films, a large quantity of a voluminous yellow precipitate also formed in solution. This was isolated by ultracentrifuging the reaction mixture.

**Growth of CdS on Substrate Prepared with Partial Self-Assembled Monolayers (SAM).** Six disks of mica were dipped in a 0.2 mM solution of octadecylphosphonic acid (OPA) prepared as previously described<sup>21</sup> so that densely packed submonolayer islands formed on the mica surface. One of the disks was separated as a control, and the other five samples were treated with fresh chemical bath solutions as described above. Mica disks were removed from the bath at 5 min and 1, 3, 6.5, and 10 h. The disks were rinsed and sonicated for 5 min in Millipore water and were then air-dried overnight before being examined by AFM.

## Results and Discussion

The components of the chemical baths used for solution growth of cadmium sulfide in this study included triethanolamine as the chelating agent, thiourea for generation of sulfide, and ammonium hydroxide as the necessary base for catalysis of thiourea hydrolysis. These reagents are similar to those reported by Sebastian et al.,<sup>18</sup> but the concentrations were varied in order to slow the reaction so that the earlier stages of deposition might be more readily observed. In particular, a lower concentration of ammonium hydroxide and a much higher ratio of triethanolamine to cadmium was used in this investigation. The typical bath composition used consisted of 0.18 M triethanolamine, 0.0059 M cadmium nitrate, 0.012 M thiourea, and 0.033 M ammonium hydroxide. The initial pH after the reagents were mixed was 10.27, and the pH remained relatively stable throughout the deposition process ( $\pm 0.05$  pH units). Rather than glass, mica was used as a substrate because of its atomically flat surface, which made it possible to more precisely distinguish features attributable to deposited materials using an AFM.

Freshly cleaved mica was placed vertically within the freshly prepared chemical bath. The solution was observed to turn yellow, and a yellow film began to form both on the mica and on the walls of the glass chamber. As the reaction progressed for longer periods of time, significant amounts of a fluffy yellow precipitate formed in solution and settled to the bottom of the chemical bath or clung to the substrates. Analysis by X-ray fluorescence spectroscopy (XRF) indicated that the elemental composition of the precipitate corresponded to that of cadmium sulfide. The XRD pattern (Figure 1) of this material showed good agreement with that of the hexagonal form of CdS, greenockite (JCPDS 41-1049), with an average crystallite size of 10 nm. There was no evidence for the cubic form of CdS, hawleyite (JCPDS 10-0454), a surprising result since Sebastian et al.<sup>18</sup> reported the growth of films that contained both the cubic and hexagonal forms of CdS using a bath of similar chemistry. While studying the preparation of monodispersed CdS using acidic solutions of cadmium salts and thioacetamide, Matijevic et al.<sup>14</sup> discovered



**Figure 1.** X-ray powder diffraction patterns of (a) CdS precipitate from the bottom of the chemical bath, (b) CdS film grown on styrene, (c) PDF line pattern of hexagonal CdS, and (d) PDF line pattern of cubic CdS.

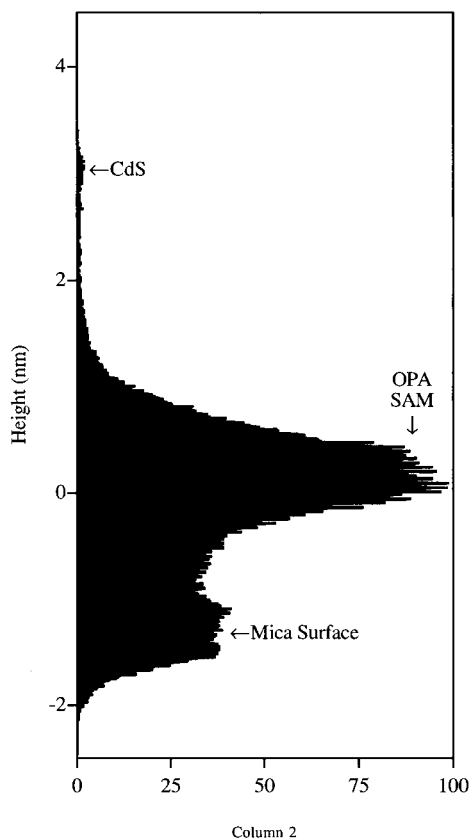
that the hexagonal structure predominated in the resulting powders. Therefore, the formation of hexagonal CdS in the present investigation may be due to the lower pH of the chemical bath. Nevertheless, other bath chemistries have also lead to primarily hexagonal films<sup>15,22</sup> as well as mixtures of cubic and hexagonal phases.<sup>15,17</sup>

The mica substrates were removed from the bath after exposure times of 3–12 min. At these short growth times, it is difficult to characterize the deposited films using typical spectroscopic techniques owing to the small amount of CdS on the mica substrate. UV/visible spectroscopy of neat films on mica shows a single peak at  $\lambda_{\text{max}} = 302$  nm, which drops to half-height by 320 nm and then trails into the visible region to almost 450 nm. The peak is first detectable in films grown for more than 10 min, and its intensity increases with time after that point. The presence of sulfur and cadmium was confirmed by their respective  $K_{\alpha 1}$  emission lines<sup>23</sup> of 2.308 and 23.176 keV detected by energy-dispersive analysis in a scanning electron microscope. The measured cadmium-to-sulfur ratios support the identification of CdS but are difficult to quantify. The sulfur  $L_{2,3}$  soft X-ray emission spectra of the deposited films also confirm their identity as CdS since they match the literature spectra<sup>20</sup> for CdS. Furthermore, there is no emission at approximately 160 eV, which would indicate the presence of elemental sulfur.

The characterization of the deposited films by X-ray diffraction (XRD) was hampered by the facts that the crystallite size of the CdS was too small to produce sharp reflections and the strongest of these reflections were coincidental with reflections due to the mica substrate. Providing that there is no epitaxial influence of the substrate on the crystalline phase adopted by the CdS film, this problem could be circumvented by de-

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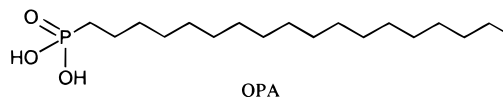
**Figure 2.** Height histogram obtained from the AFM image of mica after 1 h of CdS growth.

positing films on polystyrene foam and then dissolving away the polystyrene with toluene. The XRD pattern of the resulting material would then be expected to reflect that of the films grown on mica. The XRD pattern of the material obtained in this manner indicated that the solid contained only the hexagonal form of CdS (Figure 1). The average crystallite size, calculated from the broadness of the X-ray reflections, was determined to be approximately 7 nm.

The surface topography and projected cross-sectional views of five samples of mica subjected to solution growth of CdS were obtained by AFM. Scanning electron microscopy was useful for studying only well-developed films, since the early films were an order of magnitude thinner than the gold coating applied before SEM examinations. Height histograms obtained from AFM images were analyzed to estimate surface growth (Figure 2). In these, two peaks are visible that correspond to the CdS and the mica surface, respectively. The surface heights are reported relative to the mica surface, the position of which was estimated from the average height of the lowest peak or deepest cut of the microprobe tip and was set to  $Z = 0$ . The AFM's high-resolution allowed mapping of the first formation of islands of CdS on the surface of the mica. By 3 min, deposits had grown to a height of 4–6 Å (Figure 3). The cell parameters of hexagonal CdS are  $a = 4.1$ ,  $b = 4.1$ , and  $c = 6.7$ ; cubic,  $a = 5.8$  (ASTM). Therefore, the crystals appear to grow 1 unit cell high by 3 min, then up to 3 units high by 12 min when heights of 16–20 Å are observed. The islands were 100–400 Å across and displayed no obvious change in width over time. This indicates an initial growth of roughly 1 unit cell high

by 40 laterally, then a preference to grow upward rather than outward on the mica surface. While this is not surprising, considering the epitaxial fit of CdS for itself as compared to the mica surface, this pattern of growth has important implications to the ability to prepare coherent films by solution growth. Nevertheless, nucleation of new islands does continue as the previously formed islands increase in height as indicated by a broadening of the distribution of heights with time. Therefore, crystallization of new CdS islands on the mica surface appears to compete with epitaxial growth on the preformed islands.

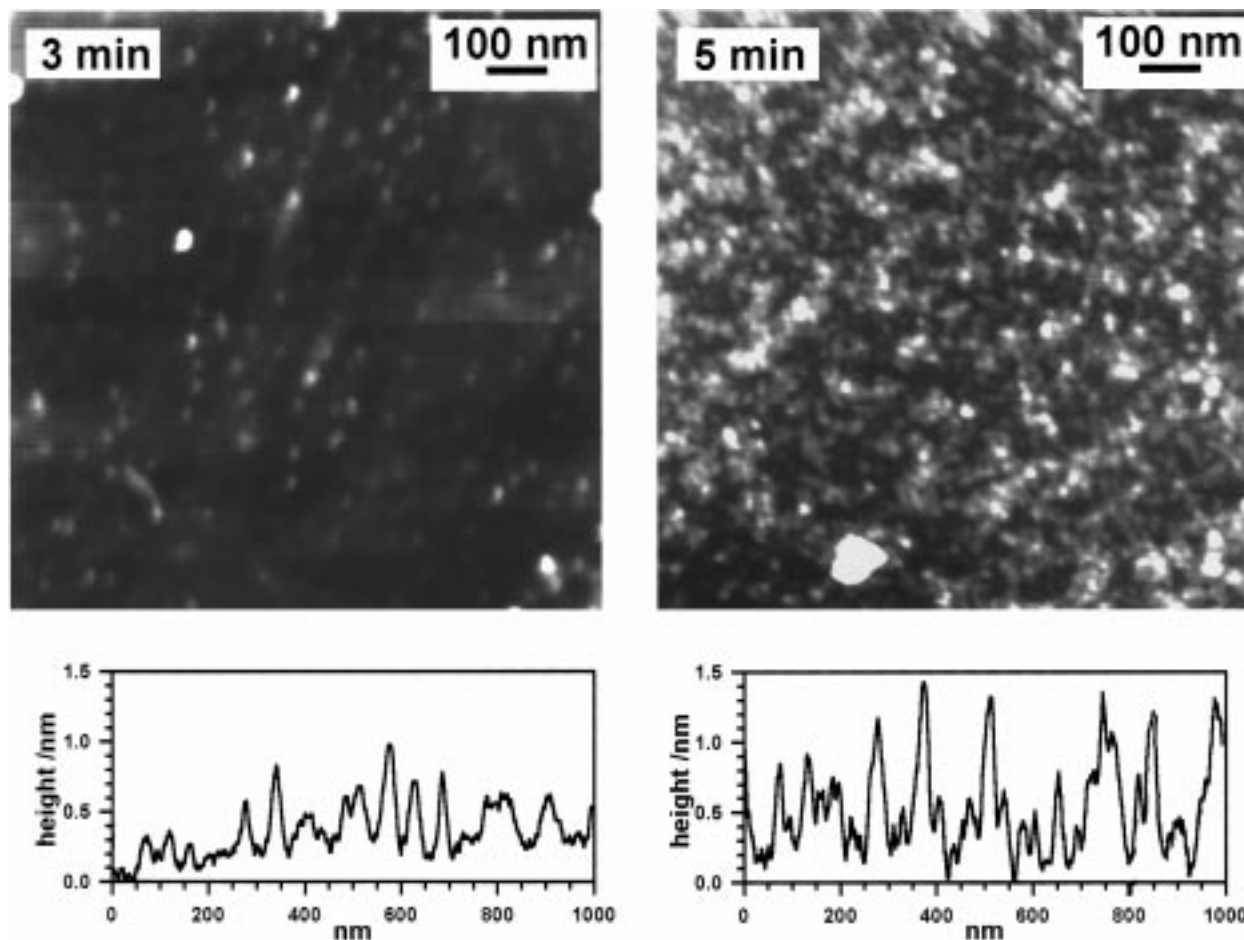
Since AFM provides only relative height values, it would not generally be possible to distinguish between bare mica and a surface covered with a smooth layer of CdS. Thus, the point that has been arbitrarily set to zero height may correspond to the mica surface but may also be due to the mica covered with several smooth layers of cadmium sulfide. It was therefore necessary to include an internal standard on the mica by treatment with a monolayer of OPA so that the true heights could be calibrated. OPA is known to form self-assembled monolayers  $18 \pm 2$  Å tall.<sup>21</sup> The partially coated disks were easily prepared by quickly dipping freshly cleaved mica into a dilute solution of the acid in THF followed by air-drying.



After CdS was solution-grown onto the monolayer-coated disk for 5 min, broad islands 16–18 Å tall of SAM were seen, along with smaller patches of CdS that were 8–12 Å tall (Figure 4 a). Peaks are visible on the histograms that correspond to the CdS, the SAM islands, and the mica surface. The CdS growth was in the range of that observed for samples without the monolayer for similar growth times. This correlation suggests that there is no initial formation of flat, featureless coatings of CdS on the mica during the early stages of growth. Therefore, the reported heights for the experiments performed without OPA are a fair representation of the early stages of growth. Notably, there was no evidence for CdS depositing on top of the OPA monolayer so that the partial SAM successfully “masked” regions of substrate during initial CdS growth. Either CdS does not bind to the monolayer or CdS attached to the monolayer has a weaker affinity for the OPA than the CdS bound directly to the mica, and it is displaced during sonication. The ability to mask the substrate using the monolayer has significant implications for novel lateral patterning techniques.

Apparently, some of the octadecylphosphonic acid was displaced during the CdS solution growth since the appearance of trilayers of OPA islands 60–65 Å tall was observed by AFM. Although nearly complete monolayer coatings of OPA can be prepared on mica without the formation of multilayered islands in THF, it is not uncommon for amphiphilic molecules of this type to rearrange in water. For example, this has been observed for Langmuir-Blodgett films of fatty acid salts.<sup>24</sup>

After 1 h of growth, the influence of the monolayer was more difficult to discern. High spots were observed



**Figure 3.** AFM images of mica without OPA monolayer after (a) 3 min and (b) 5 min of exposure to chemical bath.

in the 40–60 Å range above the surface (Figure 4b). Some of these were clearly CdS islands on the mica surface, but others jutted out of islands of monolayer. These were either trilayers of octadecylphosphonic acid, spots of CdS upon which the displaced OPA had settled, or CdS that had grown on top of OPA monolayers.

By 3 h, most of the surface was covered with CdS to a thickness of  $11.0 \pm 4.3$  nm with high spots of 15–35 nm (Figure 4c). AFM images show a surface coated with granules, 30–40 nm wide, piled on top of one another. There were random “holes” in the CdS coating, about 300–400 nm apart. OPA monolayer and bare mica could be seen through these gaps (Figure 4 d), suggesting a number of possibilities. Much of the monolayer might be displaced in the aqueous chemical bath during solution growth. The observation of trilayers after 5 min exposure to the bath suggests that this might be the case. If so, the observed “cracks” in the coating might be showing the only areas that are still covered with monolayer. On the other hand, if all the OPA monolayer is present, it must be partially, but not completely, covered with CdS (i.e. 3 h of CdS growth is not sufficient for complete coverage of the octadecylphosphonic acid islands). It is difficult to determine which of these two possibilities is correct with the data

that is currently available, but the fact that it is possible to grow films of CdS on polystyrene and polyethylene<sup>25</sup> suggests that growth of CdS on top of the hydrocarbon chains of octadecylphosphonic acid is feasible.

After 6.5 h, the reaction solution had lost most of its yellow color, the mica was tinted yellow, and a yellow powder had precipitated out of solution. AFM analysis indicated that the irregular CdS growth had leveled off at  $22.0 \pm 7.8$  nm. A broad plain of CdS covered the mica, while a few outcroppings jutted up to 60–70 nm. The results from 10 h of growth were similar, though more outgrowths jutted out of a plane  $23.5 \pm 8.2$  nm tall.

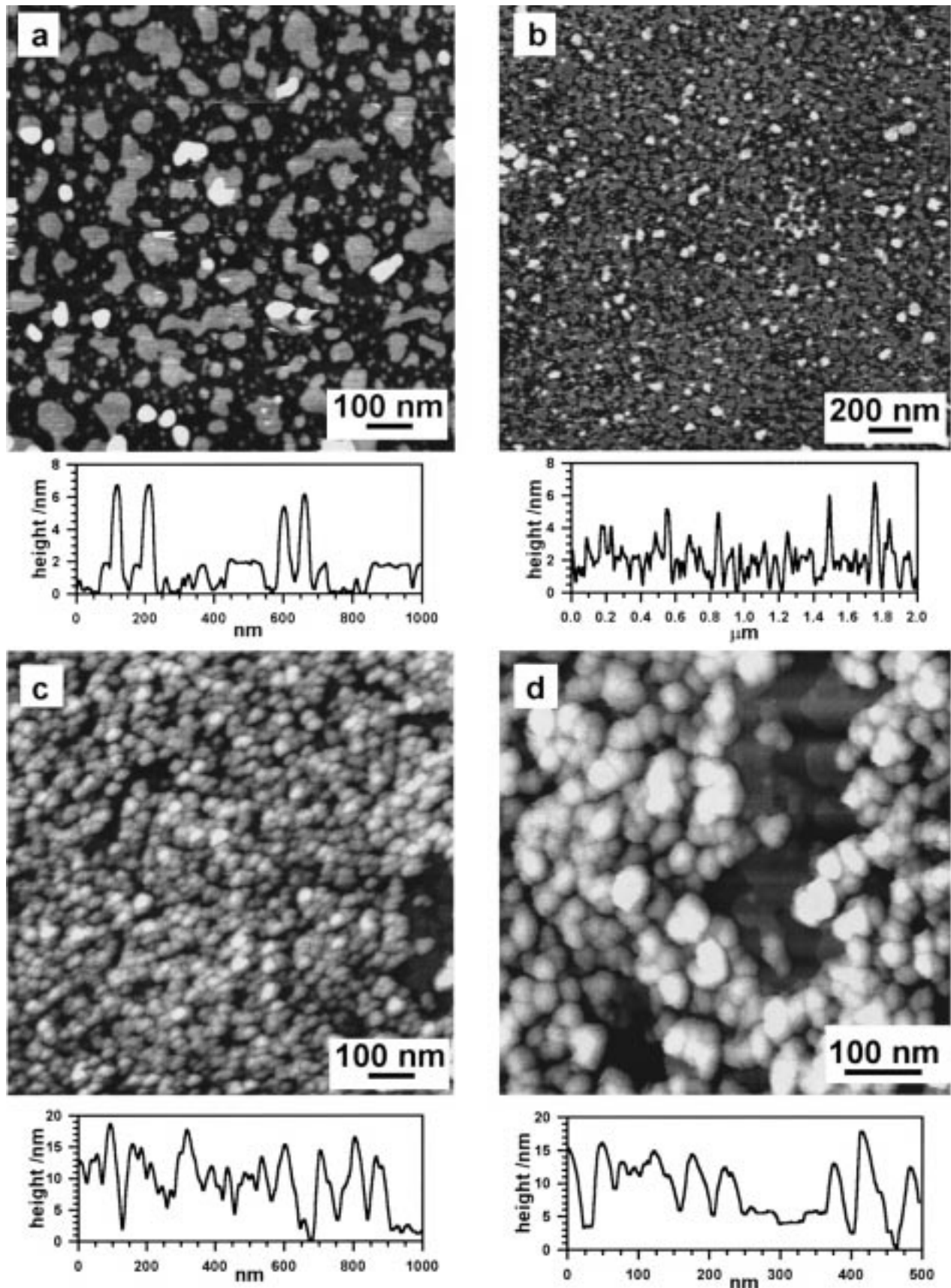
If the samples were not sonicated after removal from the reaction solution, a crystalline material was observed on the surface of the mica. This material, corresponding to the secondary film observed by others,<sup>12</sup> is likely due to CdS particles that formed in solution and then stuck to the surface of the mica. These larger, dendritic crystals grow 1–2  $\mu\text{m}$  long before branching and are observable by AFM or SEM (Figure 5).

After the longest observed growth period (16 h), AFM of the unsonicated as-deposited film demonstrated that it was still not uniform (Figure 5a). Despite the thickness of the film, a flat lower layer could be seen beneath through gaps between the branched growths (Figure 5 b). The surface of this layer was approxi-

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(25) Cadmium sulfide films on polyethylene may be readily prepared using the same chemical bath used in this investigation.

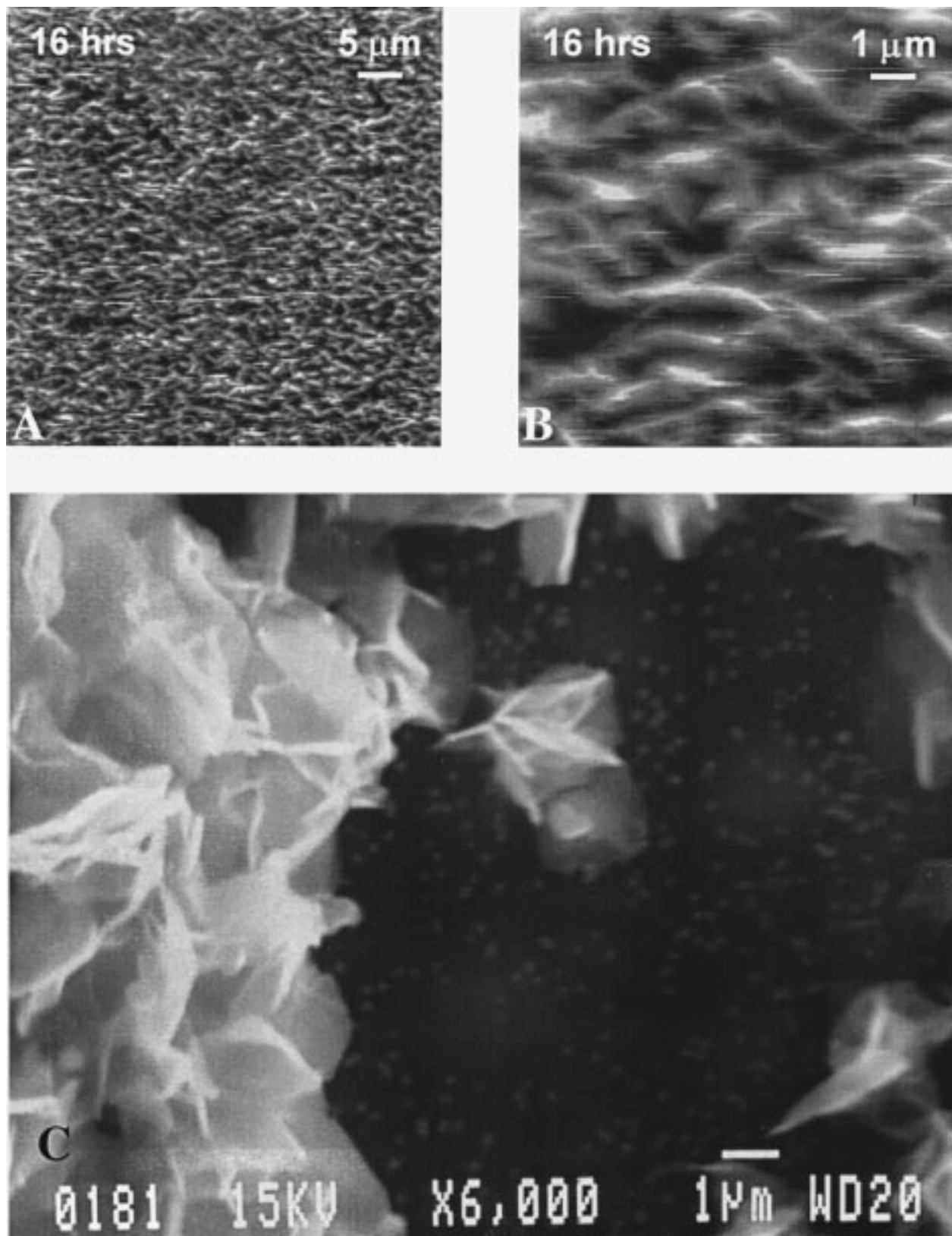


**Figure 4.** AFM images of mica with a partial self-assembled monolayer of octadecylphosphonic acid after (a) 5 min of growth, (b) 1 h of growth, and (c) 3 h of growth. (d) Close-up view of a hole present in the film obtained after 3 h of growth.

mately 22–23 nm above the mica and is covered with a few small dots of material just under  $0.1 \mu\text{m}$  wide. Those dots were about the size of the larger outcrop-

pings seen in the samples that were sonicated. The SEM micrograph of this film (Figure 5c) corroborates the AFM measurements and clearly shows a covering





**Figure 5.** Micrographs of mica after 16 h of CdS growth: (a) AFM image of secondary growth (unsonicated); (b) AFM image of secondary growth at magnification comparable to that of the SEM image; (c) SEM image showing crystals of secondary growth and primary film below.

of large, micrometer-sized dendritic crystals on top of a plane of smaller nanometer-sized islands of CdS. Presumably these islands are outcrops on an otherwise featureless (at least at the resolution of AFM and SEM) 23 nm thick ion-by-ion deposited film of CdS.

### Conclusion

Atomic force microscopy demonstrates that solution growth of CdS on mica starts as islands one unit cell high and tens of units wide. This supports an ion-by-

ion mode of deposition rather than a deposition process involving formation of colloidal CdS particles in the bulk solution. With time, the initially formed islands grow upward rather than outward on the mica surface. However, new islands of CdS continue to nucleate on the bare mica surface. Under the conditions studied, the growth levels off at a film thickness of approximately 20–23 nm. The film is not perfectly smooth and contains a few outgrowths extending up as high as 80–100 nm. After 10 h, the results of a secondary growth process, the adsorption of crystalline particulates formed in the bulk solution onto the substrate surface, is observed by AFM and SEM. The deposition of this second layer of CdS is also accompanied by precipitation of CdS onto the bottom of the growth chamber. This secondary film is not strongly adherent and may be readily removed from the substrate by sonication. However, by hindering the diffusion of free cadmium and sulfide ions to the substrate, it likely limits the extent of the more desirable ion-by-ion growth. Therefore, it is likely that the adjustment of the bath chemistry (by use of more

strongly binding chelating agents, slower generation of sulfide, etc.) so that premature precipitation does not occur will lead to formation of higher quality films by the solution-growth process.

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