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Micropatterned CdS Thin Films by Selective Solution Deposition Using Microcontact Printing Techniques

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The micropatterning of CdS thin-film on Si(100) substrate with a boundary resolution better than 100 nm was successfully obtained by a chemical bath deposition technique and microcontact printing (μCP) method using octadecyltrichlorosilane (OTS) as the organic thin layer template. The selective deposition and lift-off condition of patterned CdS thin films could be controlled by the various parameters, e.g., solution concentration, pH, temperature, and sonicating time after the deposition. When the solution concentration is moderately high ([Cd] > 0.0025 M), depositions under conditions of pH 10.5−10.7, reaction temperature 60 °C, and Cd/thiourea/ethylenediamine ratio 1/1/3 produced CdS films all over the OTS and unmodified Si surfaces. The CdS on OTS layer could be lifted off by sonication in isopropyl alcohol to produce patterned CdS films. By using solutions with low concentration, deposition of the CdS thin films occurred selectively on the unmodified Si surface and patterning could be achieved even without the lift-off process.

Introduction

The chemical bath deposition (CBD) technique to make thin films has been pursued for a long time by many researchers because this method is much less expensive and can be more easily scaled up than any other film-growing method.[1−6] Metal chalcogenide films[5] including CdS[1−4] as well as oxides and mineral films[6] have been grown by this method. Although fundamental understandings of this method such as growth kinetics and control of the morphology are still not completely achieved,[2] patterned film synthesis using this method will be also an important issue for applications. However, not much has been done with the chemical solution deposition technique toward this end.

Recently, a microcontact printing (μCP) method using organic thin layer templates such as self-assembled monolayers (SAMs) of octadecyltrichlorosilane (OTS) was introduced for micropatterning with micrometer scale resolution.[7] Patterned thin films of metals[8] and functional oxides[9−11] have been achieved by metal−organic chemical vapor deposition and by a sol−gel method. The μCP method creates micrometer scale patterns of organosilane monolayers on the substrates and modifies the printed surface of substrates, which results in selective deposition according to reaction conditions.

The combination of these two techniques would provide a way to make patterned thin films rather inexpensively. Recently, patterned ZnS and PbS thin films synthesized in this way were reported, but with low pattern resolutions.[12] Since CdS appears to be the best understood and processed material in terms of the CBD technique, we have attempted microscale patterning of CdS thin films using CBD and μCP methods.[1−3] Patterned CdS thin films with high resolution of boundary as small as 100 nm were achieved.

Experimental Section

Pattern Formation. The substrates used for the present study were Si(100) single-crystal wafers cut into 2 × 2 cm^2

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[1] (a) Forment, M.; Lincot, D. *Electrochemica Acta* **1995**, *40*, 1293. (b) Dona, J. M.; Herrero, J. *J. Electrochem. Soc.* **1997**, *144*, 4081. (c) Breen, M. L.; Woodward, IV, J. T.; Schwartz, D. K. *Chem. Mater.* **1998**, *10*, 710. (d) Lincot, D.; Ortega-Borges, R.; Fromet, M. *Philos. Mag. B, Phys. Cond. Mater. Struct. Opt. Magn. Prop.* **1993**, *68*, 185.

[2] O'Brien, P.; McAleese, J. *J. Mater. Chem.* **1998**, *8*, 2309.

[3] O'Brien, P.; Saeed, T. *J. Crystal. Growth.* **1996**, *158*, 497.

[4] Rieke, P. C.; Bentjen, S. B. *Chem. Mater.* **1993**, *5*, 43.

[5] (a) Mokili, B.; Charreire, Y.; Cortes, R.; Lincot, D. *Thin Solid Films* **1996**, *288*, 21. (b) Yamamoto, O.; Sasamoto, T.; Inagaki, M. *J. Mater. Res.* **1998**, 13, 3394.

[6] Bunker, B. C.; Rieke, P. C.; Tarasevich, B. J.; Campbell, A. A.; Fryxell, G. E.; Graff, G. L.; Song, L.; Liu, J.; Virden, J. W.; McVay, G. L. *Science* **1994**, *264*, 48.

[7] Xia, Y.; Rogers, J. A.; Paul, K. E.; Whitesides, G. M. *Chem. Rev.* **1999**, *99*, 1823 and references therein.

[8] (a) Hidber, P. C.; Nealey, P. F.; Helbig, W.; Whitesides, G. M. *Langmuir* **1996**, *12*, 5209. (b) Xia, Y.; Kim, E.; Whitesides, G. M. *J. Electrochem. Soc.* **1996**, *143*, 1070. (c) Jeon, N. L.; Lin, W.; Girolami, G. S.; Nuzzo, R. G. *Langmuir* **1997**, *13*, 3833 references therein.

[9] (a) Rieke, P. C.; Tarasevish, B. J.; Wood, L. L.; Engelhard, M. H.; Baer, D. R.; Fryxell, G. E.; John, C. M.; Laken, D. A.; Jaehnig, M. C.; *Langmuir* **1994**, *10*, 619. (b) Jeon, N. L.; Clem, P. G.; Payne, D. A.; Nuzzo, R. G. *J. Mater. Res.* **1995**, *10*, 2996. (c) Palacin, S.; Hidber, P. C.; Bourgoin, J.-P.; Miramond, C.; Fermon, C.; Whitesides, G. M. *Chem. Mater.* **1996**, *8*, 1316. (d) Collins, R. J.; Shin, H.; DeGuire, M. R.; Heuer, A. H.; Sukenik, C. N. *Appl. Phys. Lett.* **1996**, *69*, 860. (e) Marzolin, C.; Terfort, A.; Tien, J.; Whitesides, G. M. *Thin Solid Films* **1998**, *315*, 9. (f) Payne, D. A.; Clem, P. G. *J. Electroceramics* **1999**, *3*, 163. (g) Jung, D. Y.; Payne, D. A. *Bull. Kor. Chem. Soc.* **1999**, *20*, 824. (h) Aizenberg, J.; Black, A. J.; Whitesides, G. M. *Nature* **1999**, *398*, 495. (i) Koumoto, K.; Seo, S.; Sugiyama, T.; Seo, W. S.; Dressick, W. J. *Chem. Mater.* **1999**, *11*, 2305.

[10] Jeon, N. L.; Clem, P.; Jung, D. Y.; Lin, W.; Girolami, G. S.; Payne, D. A.; Nuzzo, R. N. *Adv. Mater.* **1997**, *9*, 891.

[11] Clem, P. G.; Jeon, N. L.; Nuzzo, R. G.; Payne, D. A. *J. Am. Ceram. Soc.* **1997**, *80*, 2821.

[12] Meldrum, F. C.; Flath, J.; Knoll, W. *Thin Solid Films* **1999**, *348*, 188.

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Table 1. Conditions and Results of Some Selected Deposition Reactions

reaction no.	concentration[a]			temp. (°C)	pH	saturation thickness (nm)	saturation time (min)	lift-off time (min)	remarks
	Cd	S-urea	en						
1	[Cd]/[S-urea]/[en]=1/1/2			55	10.3−10.7				powdery film
2	[Cd]/[S-urea]/[en]=1/1/3			55	10.3−10.7				conformal film
3	[Cd]/[S-urea]/[en]=1/1/3.5			55	10.3−10.7				low coverage
4	0.02	0.02	0.06	55	9.0				powdery film
5	0.02	0.02	0.06	55	10.3−10.7				conformal film
6	0.02	0.02	0.06	55	11.5				low coverage
7	0.02	0.02	0.06	35	10.3−10.7				low coverage
8	0.02	0.02	0.06	55	10.3−10.7				conformal film
9	0.02	0.02	0.06	75	10.3−10.7				powdery film
10	0.0025	0.0025	0.0075	55	10.3−10.7	63	110	2	
11	0.005	0.005	0.015	55	10.3−10.7	130	83	3	
12	0.01	0.01	0.03	55	10.3−10.7	223	70	5	
13	0.02	0.02	0.06	55	10.3−10.7	290	40	5	
14	0.04	0.04	0.12	55	10.3−10.7	290	25	7	

[a] [Cd]/[S-urea]/[en] ratio with different concentrations for rxns 1−3 and concentration in M for rxns 4−14.

pieces for μCP and CdS deposition. For the preparation of OTS organic thin-layer patterns on Si(100), the substrates were treated with a method similar to that reported by Jeon et al.[10] The Si substrate was washed with deionized water, acetone, and 2-propanol and dried with a stream of nitrogen. The dried substrate was placed in a UV/ozone generator for 30 min to remove trace organic contaminants immediately before μCP with the OTS solution. A solution of OTS in anhydrous hexane (10mM) was used as the "ink" and applied to the stamp using a spinner at 3000 rpm for 30 s. The inked stamp was contacted with the substrate by hand and held in place for 30 s. This step transfers OTS from raised regions of the stamp to the surface of the substrate applied. This procedure yields OTS thin films with approximately 30 Å mass coverage. Detailed studies of the chemical and thermal stability as a surface modifier have shown that the OTS SAMs are robust enough to withstand MOCVD (metal-organic chemical vapor deposition) up to 350 °C as well as annealing in air at 150 °C.[13] Our preliminary examination by the contact angle measurements and the AFM (atomic force microscopy) for the OTS SAM on Si substrate also confirmed the chemical and thermal stability in the solution used in this study.[14] Since the highest temperature was 80 °C and the highest pH was 11.5 in the present study, we could assume that the OTS patterns were intact during the CdS deposition process.

CdS Thin Film Formation. The OTS-patterned Si substrates were immersed in the solution containing cadmium acetate and ethylenediamine (en). The deposition of CdS commenced after the addition of thiourea (S-urea).[3] Deposited films were rinsed in deionized water, sonicated in isopropyl alcohol to remove precipitated CdS powders when necessary, and then dried with a nitrogen flow. To obtain the optimal condition for CdS deposition, parameters such as composition, pH, and deposition temperature were systematically varied as summarized in Table 1. The color of the CdS thin film changes, depending upon the thickness, from red to blue, a property which makes it easy to control the film thickness by visual inspection during the experiments.

Characterization. The quality of the film was first assessed by optical microscopy. Selected samples from the optical microscopic inspection were studied by scanning electron microscopy (SEM), profilometry, wavelength dispersive spectroscopy (WDS), Auger electron spectroscopy (AES), and X-ray diffraction (XRD). Surface profilometry (Tencor α-step 500) and scanning electron microscopy (SEM, Phillips XL30FEG) were used to determine the film thickness. Reasonably good agreement was found between the two measurement methods. The surface morphology of the CdS thin films was investigated by SEM. Depth-profiling Auger electron spectroscopy (AES, VG Scientific MicroLab 310-B, 10keV) and wavelength dispersive spectroscopy (WDS, JEOL JXA-8900R, 8keV) were used to determine the chemical composition of the prepared film in a 15 μm analysis area. X-ray diffraction data was collected on a MacScience diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å), which is operated by a 2θ scan with fixed $\theta = 1°$ to study the crystallographic orientation of the films. The lift-off of CdS thin-layer on OTS was carried out by a ultrasonic cleaner and the progress of ultrasonic treatment was observed using an optical microscope.

Results and Discussion

The successful synthesis of patterned CdS thin film on Si substrate required the optimization of the synthesis parameters such as composition, pH, temperature, and reaction time. The results from some selected reactions with various deposition conditions are summarized in Table 1. The optimum conditions for conformal film formation, en/Cd ratio of 2−3, pH 10−11, and temperature of about 50 °C, have been established by many previous researchers,[3] and our own results support these. We have varied the ratio of en/Cd and the concentration of Cd (and S-urea) from 2.5 to 40 mM while the Cd/S-urea ratio was kept at 1 (reactions 1−3 in Table 1). Increasing the en:Cd ratio above 3.5 decreased the deposition rate and resulted in Si surfaces only partially covered by CdS. When en/Cd was lower than 2.0, the reactions were very fast and produced CdS thin films with rough surfaces. As a result, the ratio of Cd, S-urea, and en was fixed at 1:1:3 in the following experiments. The optimal pH has been determined for the solution containing 20.0 mM of Cd (and S-urea) (reactions 4−6). The pH of the pristine solution was 10.5−10.7 and was adjusted by adding 0.1 N HNO_3 or 0.1 N KOH. When within the range $9.0 < pH < 11.5$, the pH of the solutions did not show any significant change after the reactions, by less than 0.3 of pH unit, and conformal films were obtained. The film deposition did not seem to be influenced by the pH in the range. When the pH was lower than 9.0, the reactions were very slow and only partially deposited films were obtained. On the other hand, the reactions were too fast for quality films when the pH was higher than 11.5. The deposition temperature was varied from 5 to 80 °C (reactions 7−9). The deposition was very slow below 40 °C. To the contrary, deposition of CdS at above 70 °C was very fast and gave rough surfaces to the thin films. Temperatures between 50 and 70 °C were determined to be appropriate for the conformal surface of CdS thin

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(13) Jeon, N. L.; Finnie, K.; Branshaw, K.; Nuzzo, R. G. *Langmuir* **1997**, *13*, 3382.

(14) Hwang, Y. K.; Woo, S. Y.; Jung, D.-Y.; Kwon, Y.-U. To be published.

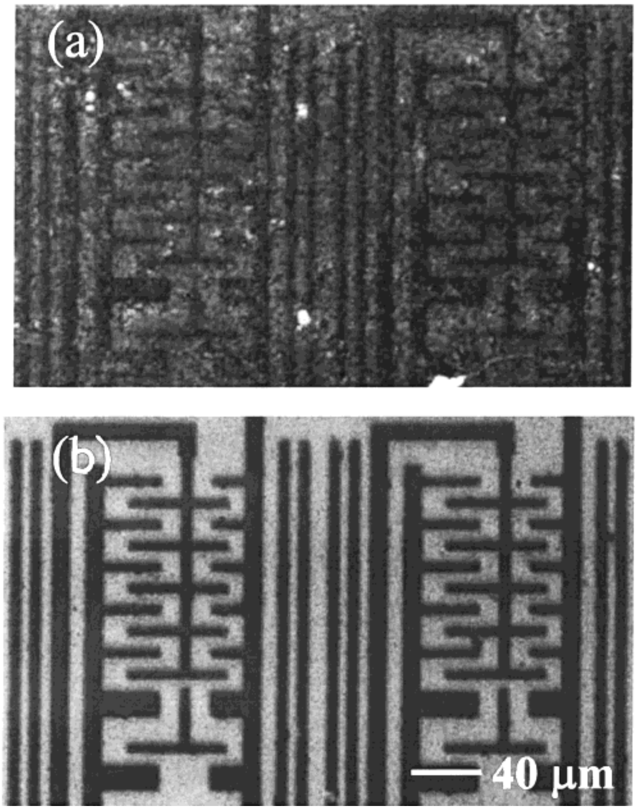

Figure 1. Optical micrographs of CdS thin film deposited on a patterned Si substrate with the conditions of [Cd] = 0.04 M, [S-urea] = 0.04 M, [en] = 0.12 M, 60 °C, and pH 10.5: (a) as deposited and (b) after lift-off via 3 min of sonication.

film by the present solution deposition technique. Therefore, the conditions we have determined to be optimal for the conformal CdS thin film on Si(100) substrate were pH 10.5−10.7, a reaction temperature of 60 °C, and a Cd:S-urea:en ratio of 1:1:3.

The reaction time is also an important parameter to obtain good surface morphology. For this, we monitored the film growth process by optical microscopy. A parallel array of about a dozen OTS-stamped Si substrates was vertically immersed in a deposition solution, and the films were withdrawn from the solution sequentially within a few minutes for microscopic inspection. Solutions with varied concentrations ([Cd] = 2.5, 5.0, 10, 20, and 40 mM) were used for this experiment (reactions 10−14). As an example, we describe our observation on the film growth under a condition of [Cd] = 5.0 mM, 60 °C, and pH = 10.5 (reaction 11). After an induction period of about 30 min, the growth of the CdS thin film starts by forming islands exclusively on the unmodified Si surface and the coverage propagates horizontally to the rest of the Si surface and eventually to the OTS-covered areas. After 83 min, whole area of the substrate was covered by CdS (Figure 1a). A patterned CdS thin film could be obtained by a lift-off through sonication for 3−5 min in 2-propanol (Figure 1b). Because of the different nucleation kinetics between the two regions of the Si surface, it should be possible to achieve selectively deposited CdS films even without the lift-off treatment by controlling the kinetic parameters. The solution concentration is an easy parameter to control for this purpose. For example, the OTS SAM patterned region of the [Cd] = 0.25 mM reaction (reaction 10) was found to be almost free of CdS deposition, while the unmodified region was almost fully covered (Figure 2). The edges of the CdS film are sharp with a resolution smaller than 100 nm. This selectivity can be explained by the saturation behavior of the film growth mechanism, which occurs because the reagents are depleted as the reaction progresses.[2] As described above, the film grows exclusively on the bare Si region initially and then propagates to the OTS SAM region. If the film growth can be stopped just before propagating to the OTS SAM region, the selective deposition can be achieved. However, because of the difficulty to fine-tune the concentration and reaction time, the patterned films so-obtained are very thin (50−60 nm thick) and often show small CdS islands on the OTS region and holes in the CdS film, as shown in Figure 2.

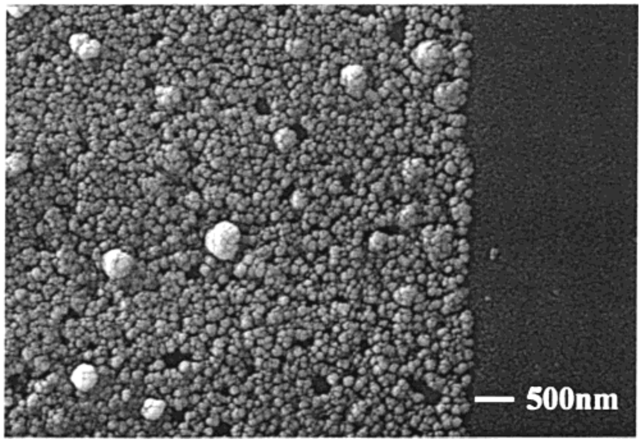

Figure 2. Scanning electron microscopic image at the boundary between OTS SAM and unmodified regions of a patterned CdS thin film synthesized with the conditions of [Cd] = 0.0025 M, [S-urea] = 0.0025 M, [en] = 0.0075 M, pH 10.5, and 60 °C.

For the other samples from higher concentrations ([Cd] > 2.5 mM, reactions 11−14), patterned CdS thin films could be obtained by sonication in 2-propanol for a few minutes. The length of the lift-off sonication treatment depends on the concentration of the solution from which the films were deposited, probably because of the different film thicknesses (Table 1). The surface profilometry scan of a so-obtained patterned film is shown in Figure 3. This scan, 500 μm in length, shows that there are three well-separated 100 μm wide and 120 nm thick CdS layers. The edges of the CdS thin film are very sharp, although the surface roughness is poor for about 40 nm of the patterned area. Apparently, the lift-off sonication process has caused mechanical damage to the CdS surface, resulting in a rough surface. The surface morphology and edge sharpness of CdS layer was studied by scanning electron microscopy (SEM) (Figure 4). This figure shows that the surface is densely covered by CdS particles with spherule shapes of average size 100−120 nm. The boundary between the CdS layer and the OTS-protected region is very sharp, in the range of less than 100 nm. The boundary resolutions of the present study are close to the best achieved by the μCP method.[11] In addition, we note that the film thickness is inversely correlated, in a qualitative manner, with the boundary resolution achieved and, thus, that thinner CdS layers enable higher resolution. We also have noted that the quality of selective deposition and the edge sharpness of the CdS thin film

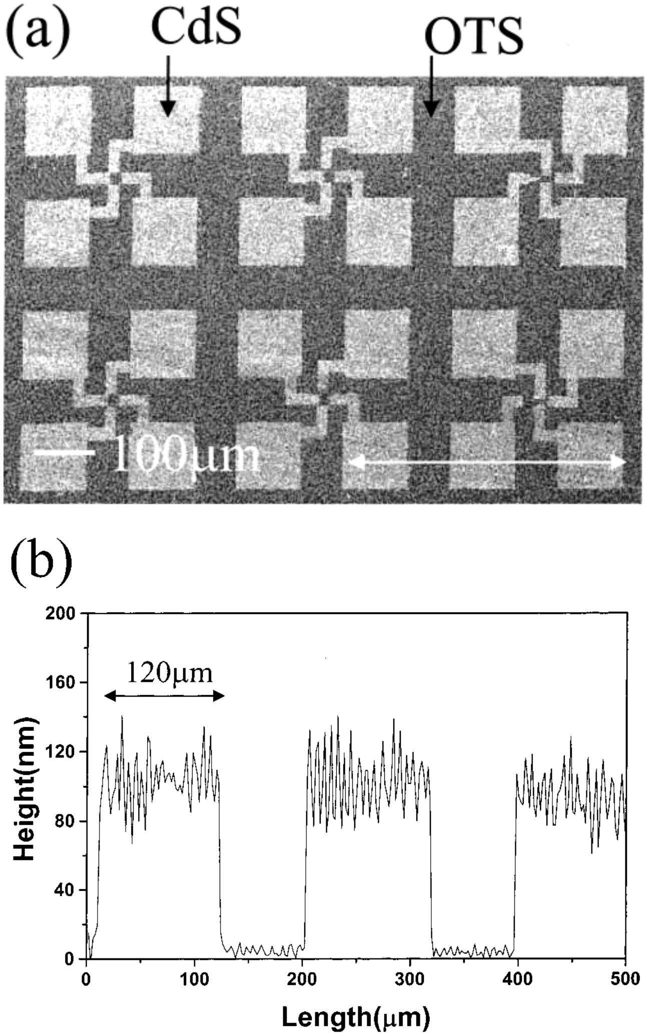

Figure 3. (a) Scanning electron microscopic image and (b) profilometry analysis plot for a patterned CdS thin film across the selected area marked in panel a. The film was synthesized with the conditions of [Cd] = 0.005 M, [S-urea] = 0.005 M, [en] = 0.015 M, 60 °C, and pH 10.5.

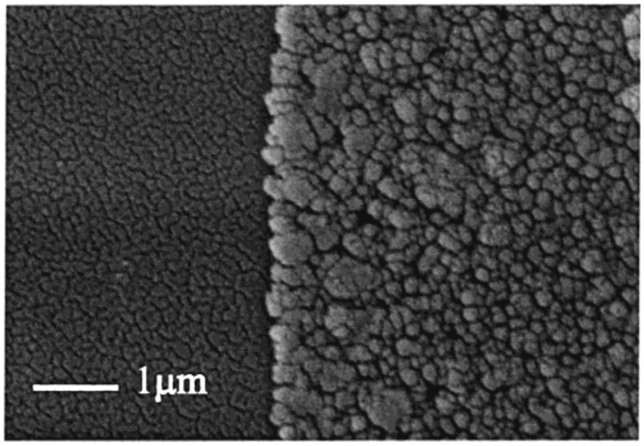

Figure 4. Scanning electron microscopic image at the boundary between OTS SAM and unmodified regions of a patterned CdS thin film synthesized with the conditions of [Cd] = 0.005 M, [S-urea] = 0.005 M, [en] = 0.015 M, pH 10.5, and 60 °C.

strongly depends on the quality of the OTS pattern transferred.[14]

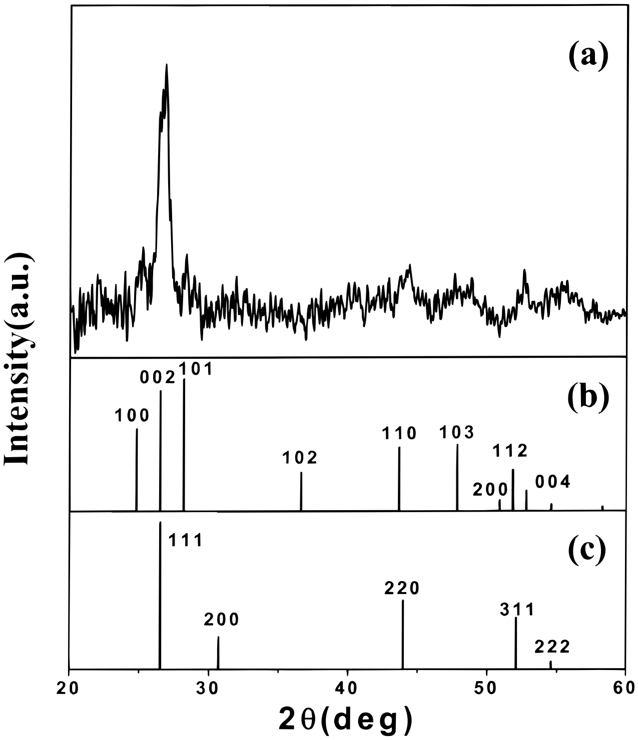

Figure 5. (a) Powder X-ray diffraction patterns of CdS thin film on Si(100) substrate synthesized with the conditions of [Cd] = 0.020 M, [S-urea] = 0.020 M, [en] = 0.060 M, pH 10.5, and 60 °C, and calculated powder X-ray diffraction patterns (b) for the hexagonal and (c) for the cubic phases of CdS.

Powder X-ray diffraction (XRD) data of the films showed peaks corresponding to both the hexagonal and cubic phases of CdS (Figure 5). Most of the literature on CdS thin films from the CBD method reported similar results, but with varied relative proportion between the two phases.[1,3,4] Our powder pattern shows strong peaks at $2\theta = 27°$ and 55°, which can be indexed as (002) and (004) of the hexagonal structure or as the (111) and (222) of the cubic structure. If these peaks are from the hexagonal phase, they imply preferentially oriented crystals with the [001] direction perpendicular to the substrate surface. However, this orientation also should have increased the intensities of the (102) and (103) peaks, which is not the case. Therefore, the powder pattern is interpreted as a mixture of both phases, with the cubic phase as the major component. This contrasts with the observations on the CdS film on styrene[1c] and carbon undercoatings[1d] and on glass substrates,[3] which showed the hexagonal phase as the major phase. On the other hand, the CdS thin film on Si substrates is reported to grow predominantly in the cubic form,[4] in agreement with our observation. Apparently, the type of substrate governs the crystal structure of the CdS deposited.

The chemical compositions of the films obtained by the wavelength dispersive X-ray spectroscopy (WDS) indicated that the films are slightly cadmium rich (Cd/S $\approx$ 1.2) as in other previous reports.[2,4] The chemical composition of CdS thin film was also studied by Auger electron spectroscopy (AES) operated at 10 keV beam voltage on a 15 μm × 15 μm analysis area after Ar^+ ion sputtering for 10 s. As can be seen in Figure 6, the CdS-covered region shows peaks for Cd and S along with O and C impurity, while the OTS-protected region shows peaks only for Si, C, and O. The relative intensity of each peak in the CdS region does not change with Ar^+

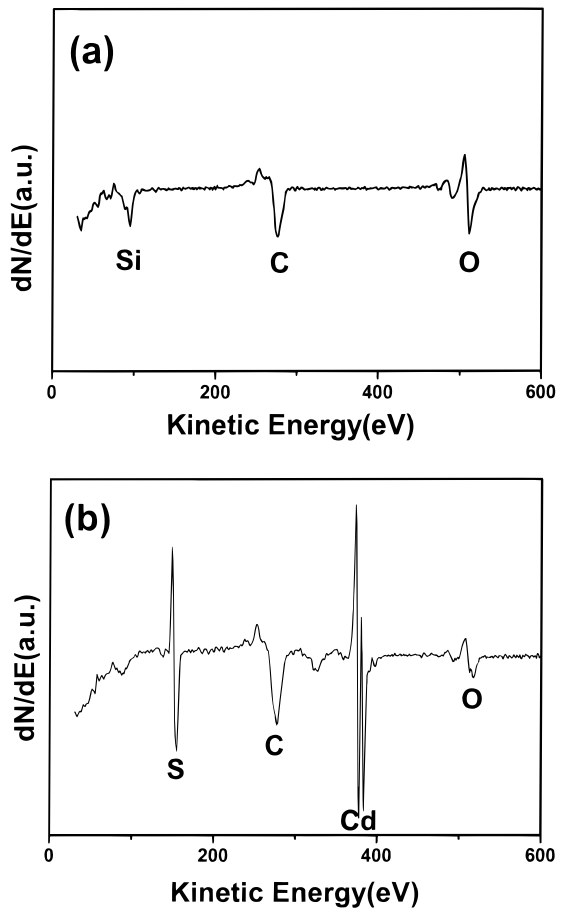

Figure 6. Auger electron spectra after 10 s argon ion sputtering of a micropatterned CdS thin film (a) for the OTS printed region and (b) for the CdS deposited area.

ion sputtering time, indicating that the composition of the CdS film is constant throughout the thickness and that the film is contaminated by C- and O-containing impurities. Carbon and oxygen impurities in the CdS layer were attributed to chemical species such as Cd$(OH)_2$, SCN^-, OCN^-, and NCN^{2-}.[15,16] Unfortunately, our data cannot tell if there is N in the film because its peak overlaps with that of Cd. This peak overlap also hinders any quantitative analysis of the Auger data for the film composition. However, the presence of impurity peaks and their assignment to anionic species corroborate with the WDS data, which indicate that the film is Cd-rich. More importantly, the AES clearly shows that our method is capable of completely selective deposition of CdS films.

Compared with the patterning of films using the μCP method in the literature, our approach is different in two aspects. While the literature examples mostly have organic underlayers in the film growth region, our system does not employ such modifications; the CdS film was directly deposited on top of a bare Si surface. This may be because of the nature of CdS, which appears to have good adherence to many different types of substrates, with the alluded $Cd(OH)_2$ underlayer probably helping the situation.[2-4] Because of this nature, only one-step μCP surface modification was needed in our case, whereas at least two-step modifications to make hydrophilic and hydrophobic regions were used in the other cases.[8-11]

In conclusion, we have demonstrated that it is possible to deposit micropatterned CdS films using the μCP and CBD techniques employing the optimized conditions for various parameters, e.g., solution concentration, pH, temperature, and lift-off through sonication after the deposition, that we have found. Despite the rather simple and straightforward procedure we have used, high selectivity and sharp boundaries were obtained. Since there are many other materials that can be deposited into films by the CBD technique,[1-6] our approach may find applications for the syntheses of patterned thin films of these materials.

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(15) Davis, L. E.; MacDonald, N. C.; Palmberg, P. W.; Riach, G. E.; Weber, R. E. (Eds.) *Handbook of Auger Electron Spectroscopy*; Physical Electronic Division, Perkin-Elmer: Eden Prairie, MN, 1978.

(16) (a) Kylner, A.; Lindgren, J.; Stolt, L. *J. Electrochem. Soc.* **1996**, *143*, 2662. (b) Kylner, A.; Wirde, M. *Jpn. J. Appl. Phys.* **1997**, *36*, 2167. (c) Niles, D. W.; Herft, G.; Al-Jassim, M. *J. Appl. Phys.* **1997**, *81*, 1978. (d) Weber, M.; Krauser, J.; Weidinger, A.; Bruns, J.; Fischer, C.-H.; Bohne, W.; Röhrich, J.; Scheer, R., *J. Electrochem. Soc.* **1999**, *146*, 2131.