

## Additive Fabrication of Patterned Multi-Layered Thin Films of Ta<sub>2</sub>O<sub>5</sub> and CdS on ITO Using Microcontact Printing Technique

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The micro-patterning of multi-layered thin films containing CdS and Ta<sub>2</sub>O<sub>5</sub> layers on ITO substrate with various structures was successfully obtained by combining three different techniques: chemical solution depositions, sol-gel, and microcontact printing ( $\mu$ CP) methods using octadecyltrichlorosilane (OTS) as the organic thin layer template. Ta<sub>2</sub>O<sub>5</sub> layer was prepared by sol-gel casting and CdS one obtained by chemical solution deposition, respectively. Parallel and cross patterns of multi-layers with Ta<sub>2</sub>O<sub>5</sub> and CdS films were fabricated additively by successive removal of OTS layer pre-formed. This study presents the designed architectures consisting of the two types of feature having horizontal dimensions of 170  $\mu$ m and 340  $\mu$ m with constant thickness *ca.* 150 nm of each deposited materials. The thin film lay-out of the cross-patterning is composed of four regions with chemically different layer compositions, which are confirmed by Auger electron microanalysis.

**Key Words :** Patterned thin films, Micro-contact printing, Multi-layer deposition, Ta<sub>2</sub>O<sub>5</sub>, CdS

### Introduction

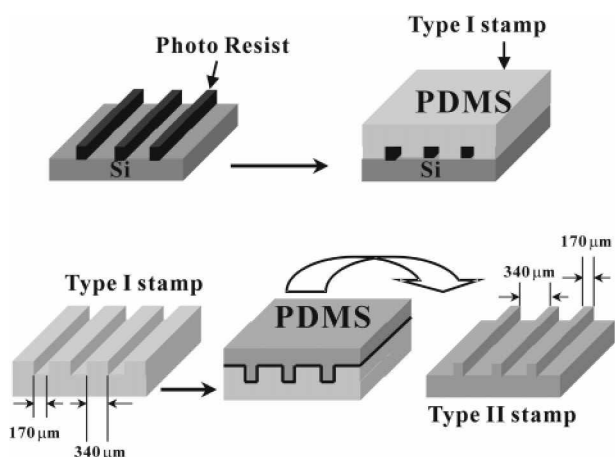
The ability to generate patterned thin-films is an important issue to modern science and technology. The fabrication of microelectronic devices is based on a sequence of physical and chemical processes, in which thin films are repeatedly deposited and etched.<sup>1</sup> Recently, self-assembled monolayers (SAMs) have begun to be explored for applications in micro-fabrication, including microcontact printing ( $\mu$ CP).<sup>2-7</sup> The patterned SAMs were used as thin resists for selective chemical etching or selective deposition. For example, applications of selective chemical etching of the patterned OTS layer demonstrate the facile fabrication of elastomeric light valve<sup>2</sup> and micro-coils on capillaries for high resolution proton nuclear magnetic resonance on nanoliter volumes.<sup>3</sup> The microcontact printing method creates micrometer scale patterns of organosilane monolayers on the substrates and modified printed surface of substrates, which results in selective deposition according to reaction conditions.

In earlier reports for selective deposition,<sup>6,8-15</sup> it has been shown that patterned SAMs of OTS, can be utilized as molecular resists to create micrometer scale patterns of organosilane monolayers on the substrates for directing the deposition of thin-films. Patterned metal thin-films of Cu,<sup>8,9</sup> Pt,<sup>10</sup> Pd<sup>10</sup> have been deposited by metal-organic chemical vapor deposition. Patterning of oxide thin-films including LiNbO<sub>3</sub>,<sup>11</sup> (Pb,La)TiO<sub>3</sub>,<sup>11</sup> and Ta<sub>2</sub>O<sub>5</sub>,<sup>12</sup> Pb(Zr,Ti)O<sub>3</sub>,<sup>6</sup> and LaMnO<sub>3</sub><sup>13</sup> has been carried out by sol-gel method. We have also shown that patterned OTS SAMs formed by the  $\mu$ CP can be combined with the chemical solution deposition (CSD) for the micro-patterning of CdS thin film<sup>14</sup> and of zeolite particles.<sup>15</sup> OTS SAMs are used in these works to functionalize surfaces with organic thin films, thereby influencing the strength of the interactions of the substrate with reagents used in the sol-gel deposition process.

In this paper, we present that the combination of these techniques (chemical solution deposition technique, sol-gel method and microcontact printing) would provide a way to fabricate multi-layered thin films with more complex architectures by using replica molding and various printing methods.

### Experimental Section

The substrates used for the present study were indium tin oxide (ITO) with 180 nm thickness prepared into 2  $\times$  2 cm<sup>2</sup> pieces on slide glass for microcontact printing ( $\mu$ CP) technique. For the preparation of OTS organic thin-layer patterns on ITO surface, the substrates were washed with deionized water, acetone, and 2-propanol and dried with a stream of nitrogen.<sup>16</sup> The dried substrates were treated with the UV-Ozone generator (high-pressure Hg lamp, 1000W) for 30-60 min to remove trace organic contaminants immediately before the microcontact printing ( $\mu$ CP).<sup>12</sup> The microcontact printing of OTS SAMs was successfully performed on ITO substrates by measuring the contact angle ( $\sim$ 105 $^\circ$ ), though the roughness (root mean square value) of ITO substrate used in this study was 4 nm as revealed by the atomic force microscope measurement. The OTS-SAMs were prepared by microcontact printing on to the ITO substrates with OTS solution in anhydrous hexane (20 mM). A solution of OTS in anhydrous hexane was used as the "ink" and applied to the stamp using a commercial 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.<sup>6</sup> This procedure yields OTS thin films with approximately 30  $\text{\AA}$  mass coverage. Two different design types of PDMS stamps were prepared for this study as shown in Figure 1. The stamp type I was made by pouring



**Figure 1.** Preparation of the PDMS stamp type I and II using replica molding technique.

a mixture of PDMS prepolymer and its curing agent (10 : 1 by weight, SYLGARD 184 kit, Dow Corning) onto a master generated from photolithography, where the thickness of photo-resist was 1  $\mu\text{m}$ . The stamp type II was also prepared by the replica molding technique onto the stamp type I, which is capable of generating similar but complementary microstructures.<sup>17</sup>

Tantalum ethoxide [ $\text{Ta}(\text{OCH}_2\text{CH}_3)_5$ , 99.98%, Aldrich] was used as the sol-gel precursor for  $\text{Ta}_2\text{O}_5$  thin film. The 0.3 M precursor solution on the basis of tantalum ethoxide was prepared by drop-wise mixing of tantalum ethoxide solution in absolute ethanol and water containing ethanol solutions. The hydrolysis ratio of water to alkoxide was 1 : 1.<sup>12</sup> The solutions were cast by spinning onto ITO substrates using a commercial spin coater (ABLE Co.). The OTS-patterned ITO substrates were flooded with 0.5 mL of 0.3 M sol precursor and spin coated two times at 3000 rpm under nitrogen gas. These films were gently polished using a cotton swab with 2-propanol at 100  $^\circ\text{C}$ . After pyrolysis of organics on a hot-plate preheated at 400  $^\circ\text{C}$ , the patterned  $\text{Ta}_2\text{O}_5$  films of approximately 170 nm thickness on ITO were obtained.

Another thin film material in the patterned multi-layers was CdS fabricated by chemical solution deposition. These substrates patterned by OTS were immersed in the solution containing cadmium acetate (Cd-Ac) and ethylenediamine (en). The deposition of CdS commenced after the addition of thiourea (S-urea). Deposited films were rinsed in D.I. water, sonicated in 2-propanol to remove precipitated CdS powders on OTS, and then dried with a nitrogen flow. To obtain the conformal CdS film with 120 nm thickness, the solution conditions were pH 10.5-10.7 at 55  $^\circ\text{C}$  for 20 min with Cd : S-urea : en ratio of 1 : 1 : 3 ( $[\text{Cd}] = 20 \text{ mM}$ ).<sup>14</sup> In our study, the selectively deposited CdS thin film with 120 nm thickness could be obtained by a lift-off through sonication for 5 min in 2-propanol using an ultrasonic cleaner.

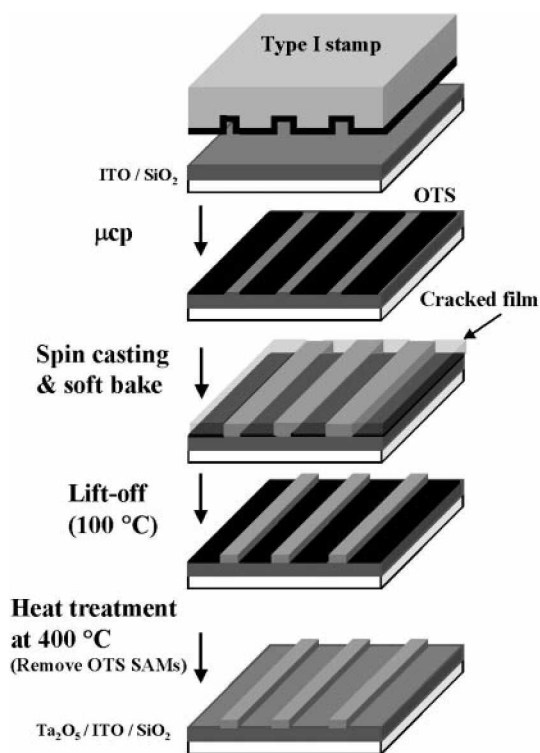
Surface profilometry (Tencor  $\alpha$ -step 500) was used to determine the film thickness and profile of the prepared patterned substrates. Auger electron spectroscopic study was

performed by using a VG Scientific MicroLab 310-B, 10 keV and the micro chemical analyses were carried out for 15  $\mu\text{m} \times 15 \mu\text{m}$  area after  $\text{Ar}^+$  ion sputtering for 10 s. Depth-profile micro-analysis was used to determine the chemical composition of the multi-layered films prepared.

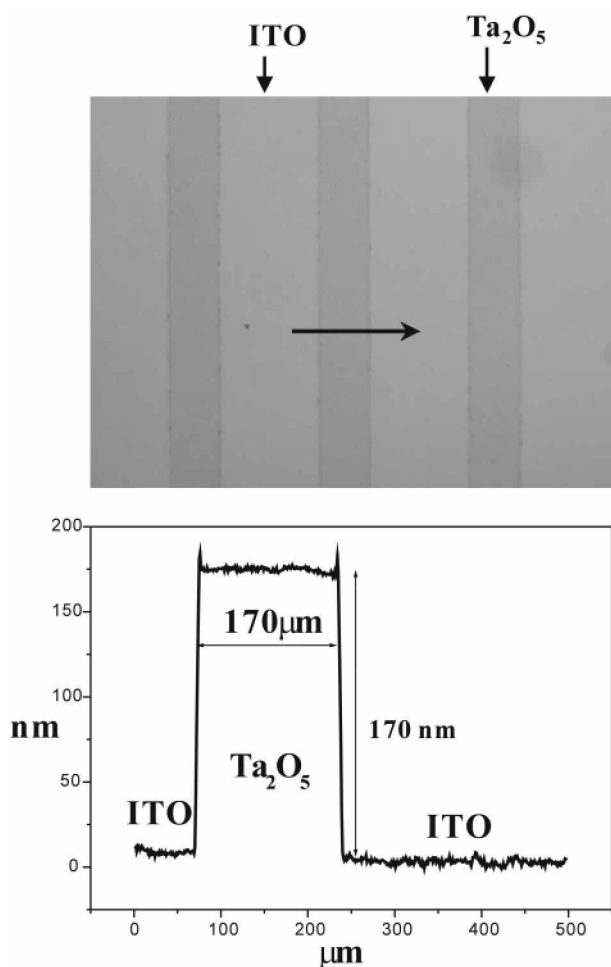
## Results and Discussion

**Selective deposition of  $\text{Ta}_2\text{O}_5$  films.** The method for selective deposition of the  $\text{Ta}_2\text{O}_5$  layers on the ITO substrate consists of several steps as shown in Figure 2: the  $\mu\text{CP}$  of OTS onto the ITO substrate, preparation of tantalum ethoxide sol solution, spin-casting onto OTS microcontact printed ITO substrates, low-temperature heat treatment, removal of delaminated oxide and a final high-temperature heat treatment to remove the OTS SAMs.<sup>12</sup> Upon heat treatment to 100  $^\circ\text{C}$ , the regions of amorphous film that formed above OTS-functionalized regions were severely cracked and could be selectively removed by mechanical polishing with a cotton swab and 2-propanol.<sup>12</sup> In this step, the stamp of type I was used to form the OTS SAMs of line shapes with 340  $\mu\text{m}$  width and finally to fabricate  $\text{Ta}_2\text{O}_5$  films of line structures with 170  $\mu\text{m}$  width.

In the preliminary examination, the OTS-monolayers applied to ITO glass were found to maintain their hydrophobic property of surfaces up to 350  $^\circ\text{C}$  for 30 min in ambient atmosphere, as determined by observation of surface wetting angle of water droplets prior to and after heat-treatment of monolayer-functionalized surfaces.<sup>18</sup> To remove the OTS-monolayers on ITO substrates and to crystallize  $\text{Ta}_2\text{O}_5$ , the



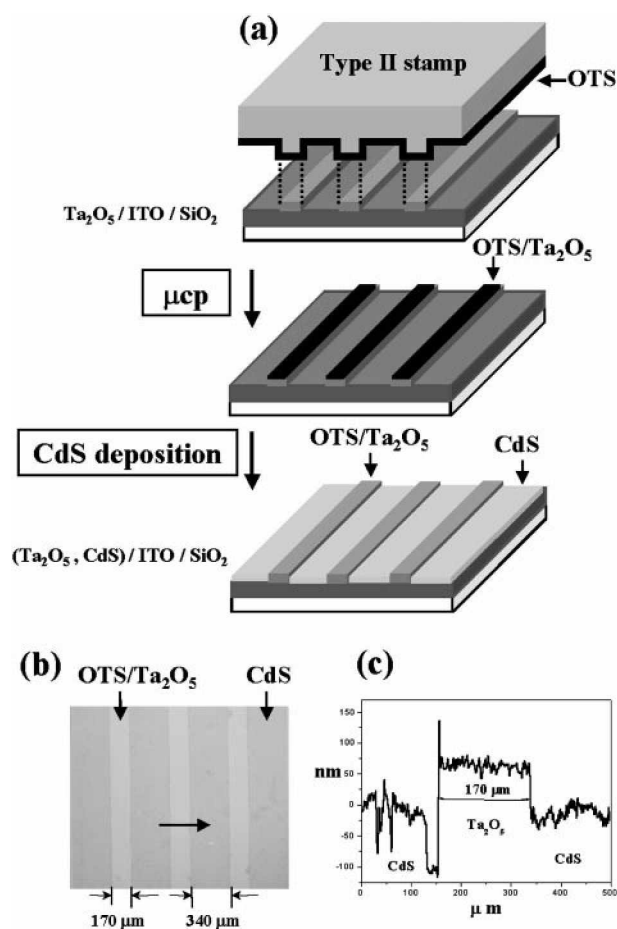
**Figure 2.** Schematic of  $\mu\text{CP}$  process for patterning of tantalum(V) oxide thin film.



**Figure 3.** Optical microscopy image and a profilometry analysis plot for a patterned  $\text{Ta}_2\text{O}_5$  thin film on the ITO substrate.

substrates were placed on a heated 400 °C hot plate for 60 min. The heat treatment eliminates OTS SAMs on ITO surface through pyrolysis in air, all the surface of the substrate becomes hydrophilic, which enables the deposition of additional thin film materials such as CdS. The X-ray diffraction data showed that the prepared  $\text{Ta}_2\text{O}_5$  thin film was amorphous after 400 °C heat treatment. In Figure 3, the surface profile of the obtained patterned film shows that the  $\text{Ta}_2\text{O}_5$  patterns are well-separated with thickness of 170 nm and width of 170  $\mu\text{m}$ . Although the lift-off process was performed by mechanical polishing with a cotton swab, the edges of  $\text{Ta}_2\text{O}_5$  thin film are very sharp, and the surface roughness is less than 20 nm in height.

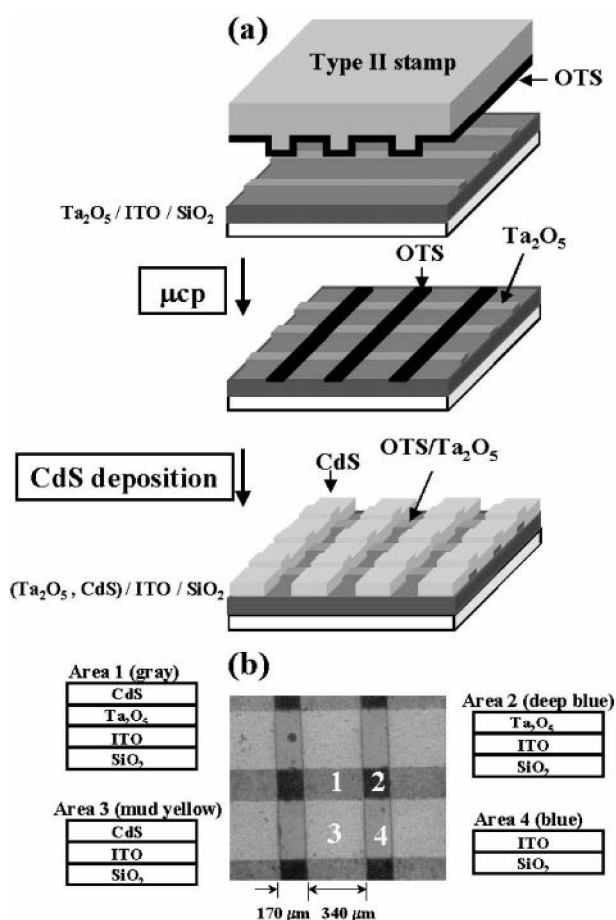
**Parallel pattern of CdS/ $\text{Ta}_2\text{O}_5$ .** The fabrication of patterned thin films containing both of  $\text{Ta}_2\text{O}_5$  and CdS layers was progressed toward the two types of features having horizontal dimensions of 170  $\mu\text{m}$  and 340  $\mu\text{m}$ . The parallel pattern of  $\text{Ta}_2\text{O}_5$  and CdS thin films was designed to produce the single type pattern which has CdS layer next to  $\text{Ta}_2\text{O}_5$  one without overlapping as shown in Figure 4. The other was the cross pattern of the two layers which involved four different layer sequences as schematized in Figure 5. For the formation of OTS SAMs onto the patterned  $\text{Ta}_2\text{O}_5$  thin film



**Figure 4.** Procedure (a), optical microscope image (b) and the profilometry analysis plot (c) of the parallel patterned multi-layers of  $\text{Ta}_2\text{O}_5$  and CdS thin film.

with 170  $\mu\text{m}$  line-width, we utilized the type II stamp prepared by replica molding technique as described in Figure 1, which has a complementary printing feature of the stamp type I.

In order to prepare a parallel pattern with  $\text{Ta}_2\text{O}_5$  and CdS thin films, the type II stamp was exactly aligned by hand or by a mechanical aligner on the  $\text{Ta}_2\text{O}_5$  line structures with 170  $\mu\text{m}$  width (Fig. 4) under an optical microscope. The printed region is the hydrophilic oxide surface of deposited  $\text{Ta}_2\text{O}_5$ , modified again with hydrophobic OTS SAMs. After microcontact printing on the  $\text{Ta}_2\text{O}_5$  line substrates, the substrates were used for the chemical deposition of CdS layer. The growth of the CdS thin film starts by forming islands exclusively on ITO region and the coverage propagates horizontally to the rest of oxide surface and eventually to the OTS-covered areas. After 20 min, the whole area of the substrate was covered by CdS and the parallel patterned multi-layers of  $\text{Ta}_2\text{O}_5$  and CdS could be obtained by a lift-off through sonication for 5 min in 2-propanol, as shown in Figure 4. Because of the different nucleation kinetics between the two regions of the substrates, it should be possible to achieve selectively deposited CdS films by the lift-off process.<sup>14</sup> Our preliminary examinations by the contact angle measurements and AFM (atomic force microscopy)



**Figure 5.** Procedure (a) and optical microscope image (b) of the cross patterned multi-layers of  $\text{Ta}_2\text{O}_5$  and CdS thin films.

show that the OTS SAM on Si substrate are chemically and thermally stable in the solution used in chemical solution deposition. Since the deposition temperature was  $80^\circ\text{C}$  and the pH was 11.5 in the previous study, we could assume that the OTS patterns were intact during the CdS deposition process.<sup>14</sup>

As a result of the sequential deposition and  $\mu\text{CP}$ , we have obtained a composite film of  $\text{Ta}_2\text{O}_5$  and CdS parallel stripes with width 170 and  $340\ \mu\text{m}$ , respectively, and each layer has different film thickness. Optical microscope image in Figure 4b showed the alignment and fidelity achieved in constructing the parallel pattern with  $\text{Ta}_2\text{O}_5$  and CdS thin films on the ITO substrate. The  $\text{Ta}_2\text{O}_5$  region is pink, and the CdS one is brown. The surface profile shown in Figure 4c indicated that the height of a  $\text{Ta}_2\text{O}_5$  thin film ( $\sim 170\ \text{nm}$ ) was higher than a CdS thin film ( $\sim 120\ \text{nm}$ ) though the edge shape was not good because OTS SAMs printing had been carried out by hand which could be improved by using the mechanical aligner. The OTS SAMs on the  $\text{Ta}_2\text{O}_5$  thin films could be removed when the sample is heat-treated at over  $400^\circ\text{C}$ .

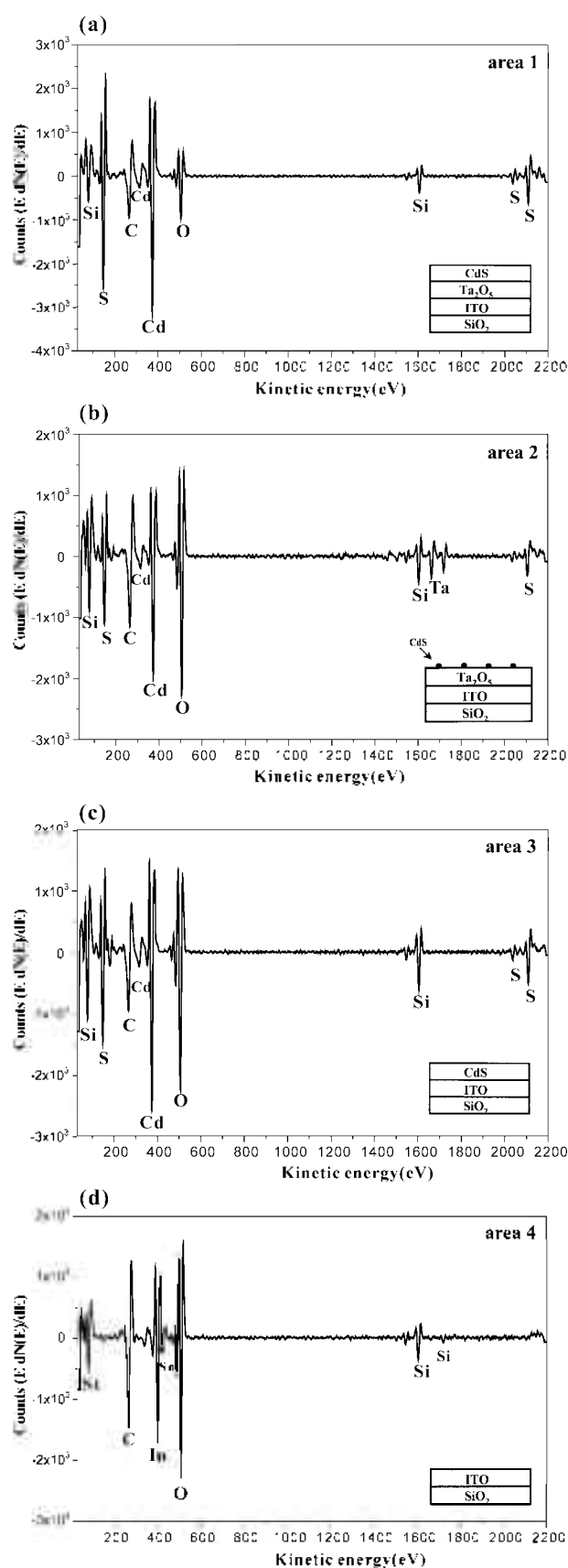
**Cross-over pattern of CdS/ $\text{Ta}_2\text{O}_5$ .** A similar procedure has been used to obtain more complex patterns of  $\text{Ta}_2\text{O}_5$  and CdS films. Figure 5a and 5b show a patterned film in which stripes of  $170\ \mu\text{m}$ -wide  $\text{Ta}_2\text{O}_5$  and  $340\ \mu\text{m}$ -wide CdS thin films crossing each other. To prepare the cross pattern of the

two different layers, microcontact printing was also performed using the type II stamp by rotating  $90^\circ$  on the ITO substrates against the line-patterned  $\text{Ta}_2\text{O}_5$  thin films, as shown in Figure 5a. The CdS thin film deposition was performed by the chemical solution deposition on the ITO substrates with the patterned  $\text{Ta}_2\text{O}_5$  thin films, using the conditions identical to those described above. As shown in Figure 5, CdS on OTS monolayers could be removed from the substrate to show bright yellow in color. The optical microscope image in Figure 5b indicates that the cross structures of the two thin films are composed of four regions of different layer compositions. The area 1 and 3 are CdS-covered regions, the area 1 and 2 are  $\text{Ta}_2\text{O}_5$ -covered regions, and the area 4 is the pristine ITO substrate with light blue color. The gray area 1, the deep blue area 2, and the mud yellow area 3 correspond to CdS/ $\text{Ta}_2\text{O}_5$ /ITO,  $\text{Ta}_2\text{O}_5$ /ITO and CdS/ITO substrate, respectively.

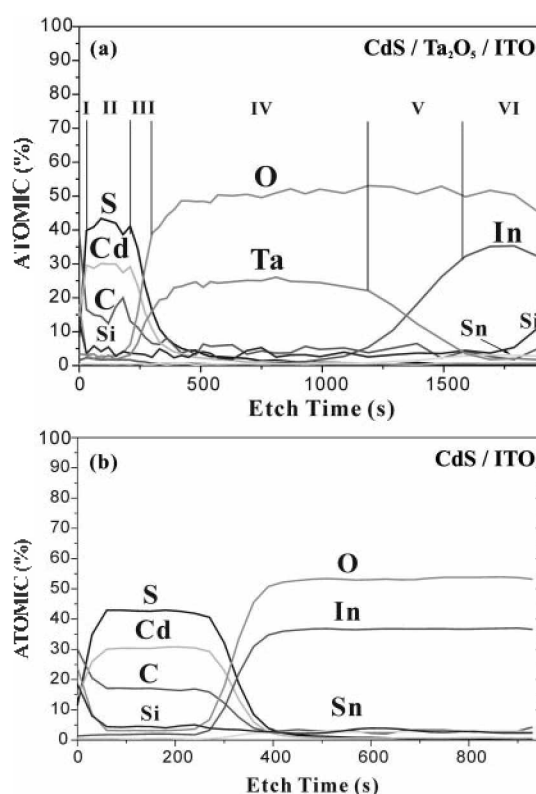
When the  $\mu\text{CP}$  step of OTS SAMs was applied onto the non-flat surface of the  $\text{Ta}_2\text{O}_5$  patterned substrates, the OTS SAMs was expected to form exclusively on the  $\text{Ta}_2\text{O}_5$  film. However, the experimental results show that the ITO region (area 4) was also printed by OTS SAMs. Consequently, the printed region was governed by the stamp used in the present study. This result is not surprising presumably because film thickness of  $\text{Ta}_2\text{O}_5$  is  $170\ \text{nm}$  much smaller than the space between two nearest  $\text{Ta}_2\text{O}_5$  films ( $340\ \mu\text{m}$ ) and the elastic stamp may easily bend. Also OTS "ink" solution layer between the stamp and substrate formed during the contact period may be considerably thick enough for the "ink" solution to reform according to the stamp feature.

The chemical compositions of each area (area 1–4) were studied by Auger electron microanalysis and are shown in Figure 6. The CdS-covered regions (area 1 and 3) showed peaks for Cd and S along with O and C impurity. In our previous studies, carbon and oxygen impurities in the CdS layers were attributed to chemical species such as  $\text{Cd}(\text{OH})_2$ ,  $\text{SCN}^-$ ,  $\text{OCN}^-$ , and  $\text{NCN}^{2-}$ .<sup>19</sup> In the area 1,  $\text{Ta}_2\text{O}_5$  layer is fully covered by CdS, which gave no Ta peak. It should be noted that the  $\text{Ta}_2\text{O}_5$  covered region (area 2) shows peaks for Ta and O along with Cd, S, O and C. Consequently, the lift-off of CdS on OTS SAMs by ultra-sonic treatment was not completed, which may be ascribed to the fact that OTS "ink" solution easily flows down to ITO region (area 1). The ITO region (area 4 in figure 5b) also shows peaks for In, Sn and O. The peak corresponding to Si in all the regions (area 1 to 4) was detected from only the surface of samples because fine particles of  $\text{SiO}_2$  were covered incidentally when the sample had been cut for the measurement.

The Auger depth profiles of area 1 and 3 in Figure 5b indicated that the compositions of CdS and  $\text{Ta}_2\text{O}_5$  films are constant throughout the thickness and that the films are contaminated by carbon containing impurities. The six zones (I to VI) in Figure 7a are interpreted as follows: in zone I the sample is original surface contaminated by absorbed species like C, CO, hydrocarbon. The zone II (CdS) and IV ( $\text{Ta}_2\text{O}_5$ ) indicated the deposited two different films. The zone III is interface between CdS and  $\text{Ta}_2\text{O}_5$  films, and the zone V is



**Figure 6.** Auger electron spectra after 10 s argon ion sputtering of a patterned multi-layered thin films; (a) and (c) for the CdS deposited regions, (b) for the Ta<sub>2</sub>O<sub>5</sub> deposited area and (d) the ITO substrate.



**Figure 7.** Depth profiles for the selective areas in the composite films; (a) CdS/Ta<sub>2</sub>O<sub>5</sub>/ITO (area 1) and (b) CdS/ITO (area 3).

interface between Ta<sub>2</sub>O<sub>5</sub> film and ITO substrate. The zone VI represents the substrate. And these depth profiles also show that CdS films are slightly sulfur-rich ( $Cd/S = 0.75$ ) and the atomic ratio of Ta : O = 1 : 2.2, as shown in Figure 7 a and b. More importantly, the AES clearly shows that our methods are capable of completely selective deposition of multi-layered patterned thin films of CdS and Ta<sub>2</sub>O<sub>5</sub> films.

## Conclusion

We have demonstrated that it is possible to deposit the various designed patterns with Ta<sub>2</sub>O<sub>5</sub> and CdS thin films by combining three methods: the microcontact printing, chemical solution deposition and sol-gel technique. Removal by thermal treatment and the additional OTS patterning by  $\mu$ CP allow us to fabricate multi-layer architectures with desired layer structures. Since there are many inorganic materials that can be deposited into films by the proposed techniques, our approach may find applications for the syntheses of complex patterned thin films of the functional materials.

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