

Reproducible Microfabrication Method for a Metal Oxide Film on a Chemical Template of Self-assembled Monolayer

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This paper presents the reproducible non-lithographic method for the microfabrication of a metal oxide film through a chemical deposition route. This method consists of three processes. First, by using a fluoroalkylsilane molecule, i.e., heptadecafluoro-1,1,2,2-tetrahydrodecyl trimethoxysilane (FAS; $\text{CF}_3[\text{CF}_2]_7\text{CH}_2\text{CH}_2\text{Si}[\text{OCH}_3]_3$), a SiO_2/Si surface was densely covered with a self-assembled monolayer (SAM) of FAS. In order to make a chemical template, the FAS-covered surface was irradiated with a vacuum ultraviolet light (VUV) with a wavelength of 172 nm for 30 min at a reduced pressure of 10 Pa through a photomask. As a result, we obtained a FAS-SAM template with alternating hydrophobic trifluorocarbon (CF_3) and hydrophilic SiO_2 monolayer (SML) regions. Next, a film of metal oxide, i.e tin oxide, was deposited on the substrate with the FAS-SAM template. Tin oxide film grew on both irradiated and unirradiated regions, but the physisorptions deposited even on the undesired region were perfectly eliminated from its surface by our developed "solution lithography", resulting a highly resolved micropattern of tin oxide film. Its pattern-resolution did not change even after the heat treatment at 600°C which is sufficient to crystallize the as-deposited film.

Key words: Micropatterning, Area-selective Deposition, Self-assembled Monolayer, Tin Oxide, Surface Tension

1. INTRODUCTION

Recent attention on tin oxide, which responds instantaneously against various inflammable and toxic gas species, has been focused in its industrial application toward a microsensor arrays for monitoring the environmental changes [1-4]. In the arrays system, the film of tin oxide allows to work as an "electronic nose". One of the requirements to achieve this goal is to develop a reliable microfabrication process that enables to place the sensing parts with each different gas-selectivity adequately onto the predefined site of the substrate surface. A number of efforts have been undertaken to improve the selectivity and sensitivity to gases by changes in doping-levels [5,6], film configuration [7], particulate shapes in film [8], and/or thickness and crystallinity of the film [9,10], but there are only a few methods with respect to the microfabrication of the gas sensing devices. In addition to post-lithography processing which is indispensable to produce a semiconductor chip, a bottom-up processing in liquid environment has recently been paid attentions. In particular, a microfabrication of metal oxide film on a chemical template of self-assembled monolayer (SAM) has been of interest to the chemists since the first demonstration by Koumoto and Dressick [11]. This method is based on area-selective deposition of metal oxide film from a liquid solution containing the desired organometallic precursors, taking advantage of the great difference in chemical reactivity between SAM-covered and -uncovered regions in the template. On the basis of their methodology, a wide variety of metal oxide films have been successfully microstructured on the predefined sites on the substrate covered with SAM templates [12-14]. Furthermore, by performing the extremely thin buffer layer of about 1 nm-thick, such SAM-templated microfabrication can be processed even on the mechanically flexible plastic sheet [15]. One of

the common problems for successful microfabrication is the unfavorable nucleation and subsequent film growth on the undesired region of the template-covered surface. Since such undesired film growth influences on the pattern resolution, it is important to eliminate selectively only the physisorptions grown on the undesired region. As in the past, several trials for this solution had been carried out [16], but they were not practically valid. In our previous study, new concept "solution lithography" was presented as a solid methodology for perfect elimination of the undesired film [10]. In this study, we compare our developed microfabrication method with the traditional one from the viewpoint of area-selectivity and the resultant pattern resolution, and discuss the value of solution lithography.

2. EXPERIMENTAL PROCEDURES

An n-type Si (100) wafer was ultrasonically washed with acetone, dichloromethane, ethanol, and Milli-Q water for each 5 min, and then photochemically cleaned by exposure to vacuum ultraviolet (VUV) light of 172 nm at a reduced pressure of 10^3 Pa for 30 min. Next, fluoroalkylsilane-SAM was formed on the cleaned substrate by chemical vapor deposition (CVD) of a FAS ($\text{CF}_3[\text{CF}_2]_7\text{CH}_2\text{CH}_2\text{Si}[\text{OCH}_3]_3$) molecule at 150°C for 3 h in a Teflon container filled with nitrogen gas. After the careful ultrasonic rinses to eliminate excess physisorbed FAS molecule, the FAS-covered sample was photolithographically micropatterned using a VUV light. The VUV-irradiation was performed for 30 min at a reduced pressure of 10 Pa through a photomask contacting its surface, directly. A SiO_2/Si substrate covered with a FAS-SAM template was immersed into a Milli-Q water containing a 0.05 mol/l of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (TCH) and heated at 60°C for 15 h. The sample was then washed ultrasonically for 30 min in absolute toluene. We have referred to this final washing

technique as “solution lithography”. Some of samples were then heated at 600°C for 3 h under ambient condition. As a control experiment, a tin oxide film was micropatterned on a FAS-SAM template using a traditional patterning method reported in elsewhere [9]. Briefly, a cleaned SiO₂/Si substrate covered with FAS-SAM template was immersed into toluene containing a 0.03 mol/l of tin chloride (TC) for 10 min at room temperature under a N₂ atmosphere, and then, was lightly washed with absolute toluene at least 5 times.

A wide variety of analytical tools were used to evaluate a FAS-SAM template and tin oxide films formed on the template as following. In order to estimate a surface tension of a FAS-SAM surface, static contact angles of three different liquids, i.e., water, methylene iodide and n-decane, were measured on sample surfaces using a contact angle goniometer. The details for this estimation are written in elsewhere [15]. Chemical and structural compositions of the samples were analyzed by Thin-film X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Micropatterns of FAS-SAM template and tin oxide films were carefully observed by a scanning electron microscopy (SEM), and an atomic force microscopy (AFM) in dynamic force microscopic (DFM), in frictional (LFM), and in Kelvin force microscopic (KFM) modes, respectively.

3. RESULT AND DISCUSSION

A FAS molecule reacts to small amounts of H₂O molecules in the container to give a hydrolyzed FAS molecule, and then attaches covalently onto SiO₂/Si via Si-O-Si linkage on the basis of dehydration and condensation mechanism (shown in Figure 1a). The chemical property of the resultant surface was studied by estimating its liquid's surface tension. The γ_s value (12.1 mN/m) estimated in this case was relatively lower than those of hydrophobic surfaces, e.g., 28.4 mN/m for toluene. This is due to much higher hydrophobic property of our prepared FAS-SAM/SiO₂/Si than the hydrocarbons. Such lower value can be mainly attributed to the low dispersion component (11.9 mN/m), and does not depend on other components, such as polar (0.1 mN/m) and hydrogen (0.1 mN/m) bonding forces. Next, we micropatterned the FAS-SAM surface to prepare its chemical template through a copper grid under a VUV irradiation at 10 Pa for 30 min. Information on surface chemical property of the FAS-SAM template was investigated by LFM and KFM, as shown in Figure 2. In LFM image (a), the microstructures of 25 × 25 μm^2 square features could be clearly imaged through the

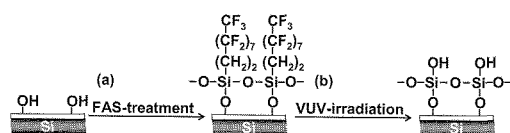


Figure 1. Schematic illustration for FAS-SAM formation and its photodegradation.

friction force contrast between the VUV-irradiated and masked regions. The VUV-irradiated and masked regions were respectively imaged as bright and dark areas when silicon cantilever covered with native oxide was used. This marked difference in friction force means that the photoirradiated regions exhibited stronger

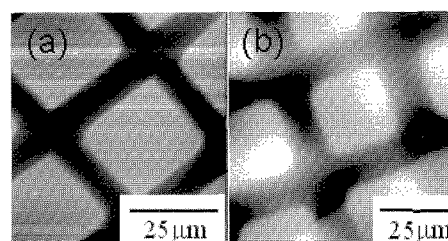


Figure 2. (a) LFM and (b) KFM images of a micropatterned FAS-SAM template surface formed on SiO₂/Si substrate by VUV irradiation for 30 min at 10 Pa through a copper mesh grid.

friction force than the unirradiated FAS-covered regions. Under exposure to VUV light in an oxygen-contained atmosphere, FAS-SAM was photooxidized and removed by VUV-activated oxygen species. As a result, a bottom part of the FAS molecule which is consisted of 0.2–0.27 nm thick SiO₂ monolayer (SML) remains on the substrate surface (Figure 1b). Since SML surface exhibits highly hydrophilic nature with a water-contact angle of 5° or less, a silicon cantilever covered with native oxide adheres strongly to the SML surface. The friction force contrast on the VUV-irradiated regions was thus greater than that on the FAS-covered surface. As a result, the SML regions are imaged as bright areas than the FAS-covered regions. In KFM image (b), VUV-irradiated regions, that is, SML regions are imaged as brighter areas than masked regions, that is, FAS-SAM regions. In principle, bright areas in KFM image indicate a positive surface potential than that of dark areas [17]. Since the surface potential contrast between the SiO₂/Si substrate covered and uncovered with SAM is attributable to the dipole moment of the SAM, a FAS-SAM region should be practically imaged as dark area than the SML region as shown in Figure 2b [18]. As is evident from both images, on the FAS-SAM surfaces, we could not find any great difference in contrast, indicating that the unirradiated regions were uniformly and densely covered with FAS molecule. Thus, we concluded that this micropatterned surface was

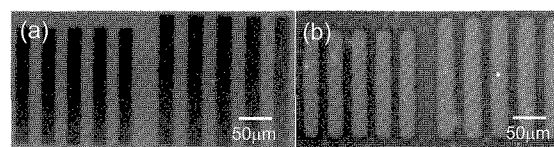


Figure 3. SEM images of (a) a photomask and (b) a TC thin film deposited on FAS-SAM template fabricated by a VUV irradiation through the photomask.

enough to work as a chemical template.

Employing the suitable FAS-SAM template as shown in Figure 2, thin films were deposited on the templates in each solution of TC and TCH. Figure 3 shows the SEM images of (a) a photomask and (b) a typical micropattern of a thin film deposited in TC solution. In the image of (a), the bright and dark areas show masked, i.e., FAS-covered, and VUV-irradiated, i.e., SML, regions, respectively. As can be seen in the image of (b), rectangle structures of 25 × 250 μm^2 were imaged, due

to preferential growth of films on the SML regions. The thickness of the resultant microstructured film was about 21.2 nm. As an edge feature of the microstructures was relatively sharp, we estimated the variation by measuring the line widths at 20 equally spaced points on each micropattern in the image (b) using the method reported in elsewhere [11]. The average of the line width was about 33.6 μm , and the rectangle edge roughness was estimated to be 8.6 μm by the standard deviation of the line width. This represents a 25.6% variation, i.e., 8.6/33.6, in the nominal line width, being larger than the usual 5% variation afforded by current microelectronics design rules. This traditional patterning method takes advantage of great difference in chemical reactivity between FAS- and SML-covered regions. First, a TC molecule hydrolyzes by reacting with very small amounts of H_2O molecule adsorbed on the SML surface, and then reacts with SiOH group to give a Sn-O-Si covalent linkage. Subsequent film growth progresses on the SnOH surface through dehydration and condensation manner to form TC film. In contrast, a nucleation on FAS-covered regions does not occur for a certain time even after nucleation and subsequent film growth on the SML surface, due to insufficient H_2O molecule for hydrolysis of TC molecule on super-hydrophobic FAS regions. As a result, area-selective growth of TC film can be achieved as shown in Figure 3b. However, further immersions (> 10 min) in TC solution made the microstructure in pattern resolution deteriorate. Figure 4 shows a XPS survey spectrum of a FAS-covered sample immersed in a 0.03 mol/l of TC solution. As clearly seen, the C_{1s} , Si_{2s} , Si_{2p} , O_{1s} , and Sn_{3d} peaks could be observed at around 285 cm^{-1} , 151 cm^{-1} , 99 cm^{-1} , 534 cm^{-1} , and 489 cm^{-1} , respectively. This result of analysis demonstrates

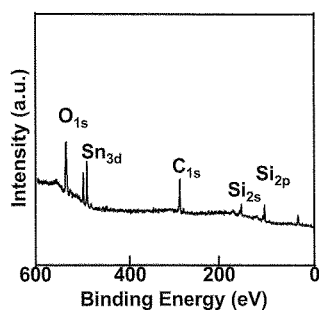


Figure 4. XPS survey spectrum of a FAS-SAM/SiO₂/Si immersed in a toluene containing of a TC molecule under N₂ atmosphere.

the undesired growth of a TC film even on the inert FAS-covered surface. Due to the reaction of a TC molecule with H_2O dissolving even into toluene, a number of TC particles homogeneously nucleate in its solution with increasing immersion time, and then physically adsorb entire over the template surface without selectivity. Such physisorbed precipitate plays a role on a new nucleation site. In order to avoid the undesired growth of the film, the condition for film growth must be strictly regulated, but in practice it had been impossible to grow the relative-thick film with keeping area-selectivity.

To achieve a perfect area-selectivity of the structure,

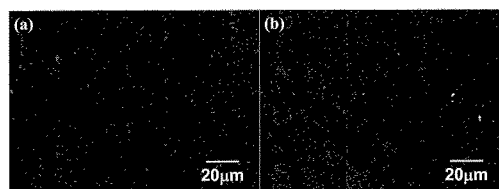
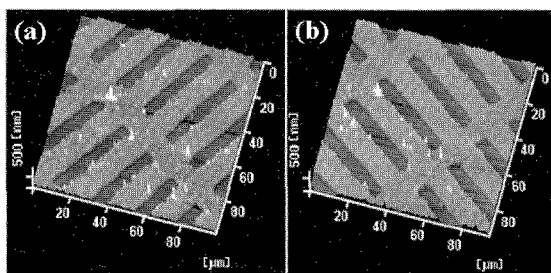


Figure 5. SEM images of the surfaces of a TCH-film/FAS-SAM-template/SiO₂/Si sonicated for (a) 0.5 min and (b) 30 min.

we noticed an interfacial chemical property between the undesired film and the FAS-covered surface. Due to the densely packed trifluorocarbon groups of FAS-SAM, the formed heterogeneous interface must exhibit the highly hydrophobic property. When we sonicated a TCH-covered FAS-SAM sample in absolute toluene for 30 min, the TCH film was perfectly eliminated, evidently from XPS analysis. As a control experiment, we sonicated another TCH-covered FAS-SAM sample with Milli-Q water, but the film remained tightly and could not be removed from the FAS-SAM surface. This marked difference in film's stability against each solvent correlates deeply with the interfacial chemical property between TCH film and FAS surface. Due to the hydrophobicity similar to trifluorocarbon group, absolute toluene can easily come into the heterogeneous interface, and remove only the physisorbed film from the FAS-SAM surface. In contrast, the super hydrophilic solvent, i.e., Milli-Q water, is not allowed to come into the hydrophobic FAS-formed interface. Alternatively, Milli-Q water attacked to the outermost surface of the hydrophilic TCH film formed on FAS-SAM. Actually, prolonged sonication in Milli-Q water caused the destruction of both films on the SML- and the FAS-covered surfaces. In order to make a clear-cut observation of the elimination, a TCH film was deposited on a substrate covered with FAS-SAM template, and the sample was then sonicated in absolute toluene. The TCH film on FAS-covered regions started to destroy just after the sonication (Figure 5a), and was perfectly removed at 30 min as shown in Figure 5b. In contrast, the TCH film remained intact on SML surface of FAS-SAM template even after the sonication. This evidently indicates that the TCH film grown on the SML region stayed tightly fixed to the surface through an interfacial Sn-O-Si covalent linkage, while the films deposited on the FAS-covered regions had been physically adsorbed, and thus completely eliminated by sonication [10]. Changes in thickness of the remained film after the elimination were measured to be within 8%, indicating that dehydration and condensation could proceed well to form Sn-O-Sn covalent linkage in the film. Actually, Thin-film XRD revealed that the TCH film was composed of crystalline of tin oxide with cassiterite phase. For quantitative evaluation in pattern-resolution of the resultant micropattern, we measured the pattern width at 20 equally spaced points on each rectangle pattern in Figure 6a. The average width of each pattern in this image is about 10.6 μm . The pattern edge roughness was measured to be about 0.32 μm . Thus, the variation in the nominal pattern width was estimated to be less than 5% (i.e., 0.32/10.6 \times



100), which satisfies much sufficiently the requirement

Figure 6. DFM images of (a) unannealed and (b) annealed micropatterns of TCH films formed on FAS-SAM templates. The annealing was carried out at 600°C in an ambient air.

for current microelectronic design rule. Finally, we investigated thermal influences on thickness, area-selectivity, and pattern-resolution of the microstructured TCH film by annealing the sample at 600°C, which is a crystallization temperature of cassiterite phase [9]. As clearly seen in Figure 6b, the micropatterns could be observed area-selectively on the SML regions, while the surrounding FAS-covered regions were free of deposits even after crystallization. Thus, high pattern resolution was also maintained even after annealing, when compared Figure 6a with 6b. Thickness of micropatterned film became slightly thin after crystallization, because of thermal shrinkage with increasing crystalline degree. Thus, the soft lithographic method demonstrated here has a general versatility to microfabricate metal oxide films.

4. SUMMARY

We demonstrated an advantage of our developed solution lithographic method to fabricate the highly resolved micropattern of a metal oxide film through an aqueous route. Importantly, using our microfabrication method, the perfect area-selectivity and high pattern resolution could be unchanged even after annealing for their crystallizations. Our technique, presented here, offers a further advantage in that by selecting an appropriate deposition time the microstructures' thickness can be freely controlled over the range of several nanometers to over several μm without any marked change in either morphology or resolution. This is in marked contrast to traditional microfabrication processing obtained with liquid phase processes, where the target materials generally deposited not only on the predefined regions, but also on undesired regions with increasing immersion time, resulting in a decrease of pattern resolution. In such cases, film thickness had to be strictly regulated to ensure area-selectivity. However, our solution lithographic microfabrication method allows the complete elimination of the physisorbed deposits on the undesired regions. Thus, precise thickness control is not absolutely necessary. That is, a variety of chemical deposition routes are available to microfabricate metal oxide films. By selecting an appropriate precursor solution, our microfabrication method demonstrated here can be applied to various metal oxides other than tin oxide.

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5. REFERENCES

- [1] C. Hagleitner, A. Hierlemann, D. Lange, A. Kummer, N. Kerness, O. Brand, and H. Baltes, *Nature*, 2001, 414, 293-296
- [2] W. Göpel, and K. D. Schierbaum, *Sens. Act. B*, 1995, 26-27, 1-12
- [3] A. I. Kingon, J. -P. Maria, and S. K. Streiffer, *Nature*, 2000, 406, 1032-1038
- [4] R. E. Baby, M. Cabezas, E. N. W. de Reça, *Sens. Act. B*, 2000, 69, 214-218
- [5] L.A. Patil and D.R. Patil, *Sens. Act. B*, 2006, 120, 316-323
- [6] E. Comini, A. Vomiero, G. Faglia, G. Della Mea and G. Sberveglieri, *Sens. Act. B*, 2006, 115, 561-566
- [7] N. S. Ramgir, Y. K. Hwang, S. H. Jhung, H. -K. Kim, J. -S. Hwang, I. S. Mulla and J. -S. Chang, *Appl. Surf. Sci.* 2006, 252, 4298-4305
- [8] L. Vayssieres, and M. Graetzel, *Angew. Chem. Int. Ed.*, 2004, 43, 3666-3670
- [9] N. Shirahata, Y. Masuda, T. Yonezawa, K. Koumoto, *Langmuir*, 2002, 18, 10379-10385
- [10] N. Shirahata, W. Shin, N. Murayama, A. Hozumi, Y. Yokokawa, T. Kameyama, Y. Masuda, K. Koumoto, *Adv. Funct. Mater.* 2004, 14, 580-588
- [11] K. Koumoto, S. Seo, T. Sugiyama, W. S. Seo, W. J. Dressick, *Chem. Mater.* 1999, 11, 2305.
- [12] Y. Masuda, W. S. Seo, and K. Koumoto, *Langmuir* 2001, 18, 4876-4880
- [13] T. Nakanishi, Y. Masuda, and K. Koumoto, *Chem. Mater.* 2004, 16, 3484-3488
- [14] Y. Gao, M. Nagai, Y. Masuda, F. Sato, and K. Koumoto, *J. Cryst. Growth* 2006, 286, 445-450
- [15] N. Shirahata and A. Hozumi, *Chem. Mater.* 2005, 17, 20-27
- [16] N. Shirahata, W. Shin, N. Murayama, Y. Masuda, K. Koumoto, *J. Ceram. Soc. Jpn.* 2004, 112, S562-S566.
- [17] H. Sugimura, K. Hayashi, N. Saito, N. Nakagiri, and O. Takai, *Appl. Surf. Sci.* 2002, 188, 403-410
- [18] K. Hayashi, N. Saito, H. Sugimura, O. Takai, and N. Nakagiri, *Ultramicroscopy* 2002, 91, 151-156

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