Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of the European Ceramic Society 24 (2004) 301–307

www.elsevier.com/locate/jeurceramsoc

Site-selective deposition and micropatterning of tantalum oxide thin films using a monolayer

Yoshitake Masuda*, Shinichi Wakamatsu, Kunihito Koumoto

Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan

Accepted 23 March 2003

Abstract

We developed a novel process to fabricate a micropattern of tantalum oxide thin film on a patterned self-assembled monolayer (SAM) using the gradual hydrolysis reaction of tantalum ethoxide. SAM of octadecyltrichloro-silane (OTS) was prepared on a Si substrate from an OTS solution. The OTS-SAM was irradiated with UV light through a photomask to form methyl group and silanol group patterns on a substrate. The patterned OTS-SAM was then immersed in a tantalum ethoxide solution to selectively deposit thin films on silanol group regions. Site-selective deposition of amorphous tantalum compound was realized and a micropattern of the thin films was successfully fabricated at room temperature. The thin film was characterized to have the composition, $Ta_2O_5{\cdot}4H_2O$ ($Ta_2O(OH)_8$) by XRD, XPS, FT-IR and TG-DTA. The amorphous thin film transformed into crystalline Ta_2O_5 after annealing at 800 °C for 2 h in air. The feature edge acuity of the micropattern remained unchanged by the annealing and thus a micropattern of Ta_2O_5 thin film was successfully fabricated.

Keywords: Micropatterning; Self-assembled monolayer; Site-selective deposition; Ta_2O_5; Films

1. Introduction

Tantalum oxide has received considerable attention as a protective coating material for chemical equipment,[1] optical decices,[2] a suitable material for storage capacitors in very large scale integrated circuits,[3–5] etc. Accordingly, fabrication of thin films and micropatterns of tantalum oxide look very promising for applications in future devices.

Payne et al.[6] fabricated a micropattern of tantalum oxide thin film from a sol-gel solution using a lift-off process. A patterned self-assembled monolayer (SAM), which has octadecyl group regions and unfunctionalized regions, was prepared using microcontact printing (μCP). Sol-gel precursors of tantalum ehoxide [$Ta(OCH_2CH_3)_5$] were spin coated on a whole substrate of patterned SAM and heated at 300 °C. The substrate was then polished to remove deposited thin films on octadeyl groups regions, which adhered weakly to octadecyl groups compared to their adherence on unfunctionalized regions. The micropattern of amorphous films was thus fabricated. The micropattern was converted into crystalline Ta_2O_5 thin films by annealing at 700 °C. This process expertly employed the interaction between deposited films and substrate surfaces. The feature edge acuity of this pattern is expected to be further improved by modification of the deposition process to realize site-selective deposition.

We have reported a novel process to fabricate a micropattern of TiO_2 thin film on a patterned SAM.[7–9] TiO_2 thin films were formed on silanol group regions of a SAM through the hydrolysis reaction of the titanium precursor. Surface interaction between the titanium precursor and functional groups on the substrate surface was used to realize direct site-selective deposition of TiO_2 thin films. The feature edge acuity of the TiO_2 micropattern reached was well below the electronics design rule, 5%. However, sensitive interactions between precursors and surface functional groups of a substrate are employed for molecular recognition in the site-selective deposition process. This sensitivity makes it difficult to apply the process to other materials.

In this paper, we realized direct site-selective deposition and a micropattern of tantalum oxide thin films on

* Corresponding author. Tel.: +81-52-789-3329; fax: +81-52-789-3201.
E-mail address: masuda@apchem.nagoya-u.ac.jp (Y. Masuda).

0955-2219/03/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0955-2219(03)00230-9

a patterned SAM using a controlled hydrolysis reaction of the tantalum precursor. SAM of octadecyltrichlorosilane (OTS) was prepared by immersion of a silicon substrate in an OTS solution. The OTS-SAM was irradiated with UV light through a photomask to form a pattern of octadecyl group regions and silnaol group regions. The patterned SAM was then immersed in a solution containing tantalum ethoxide to selectively deposit amorphous thin films on the silnaol groups. Consequently, a micropattern of tantalum oxide was successfully fabricated through direct site-selective deposition. The deposited films were further crystallized by annealing at 800 °C to form a micropattern of crystalline Ta_2O_5 thin films.

2. Experimental

The OTS-SAM was prepared by immersing the p-type Si (100) wafers in an anhydrous toluene solution containing 1 vol.% OTS for 5 min in a N_2 atmosphere.[10–17] The SAMs were exposed for 2 h to UV light (184.9 nm) from a Hg lamp (low-pressure mercury lamp, NL-UV253, Nippon Laser & Electronics Lab.) through a mesh for transmission electron microscopy. The UV-irradiated regions became hydrophilic due to Si–OH group formation, while the non-irradiated part remained unchanged, i.e. it was composed of hydrophobic octadecyl groups, which gave rise to the patterned OTS-SAM.[18–21] In order to check for successful film formation and functional group change, water drop contact angles were measured for both the irradiated and non-irradiated surfaces. The initially deposited OTS-SAM showed a water contact angle of 96°, but the UV-irradiated surface of SAM was wetted completely (contact angle $< 5°$). The water contact angle of the OTS-SAM was slightly lower than the reported values (111–115°).[18,22]

The surface morphology of the deposited films was observed using a scanning electron microscope (SEM; S-3000N, Hitachi Ltd.). The thickness of the films was estimated using an atomic force microscope (Nanoscope E, Digital Instruments) and an ellipsometer (ESM-1, ULVAC Inc.). The thin films were evaluated using XPS (X-ray photoelectron spectroscopy, ESCA-LAB 210, VG Scientific Ltd., $1-3\times10^{-7}$ Pa). The X-ray source (MgK_α, 1253.6 eV) was operated at 15 kV and 18 mA. The thin films were further evaluated by Fourier-transform infrared spectroscopy (FT-IR 610, JASCO Co., Ltd.). Thermogravimetric analysis (TG) and differential thermal analysis (DTA) of the deposition were conducted (Thermo Plus TG8120, Rigaku). Crystallization was evaluated using an X-ray diffractometer (XRD; RAD-C, Rigaku) with CuK_α radiation (40 kV, 30 mA) and a Ni filter plus a graphite monochromater.

3. Results and discussion

3.1. Site-selective deposition and micropatterning of $Ta_2O_5{\cdot}4H_2O$ thin films on SAM

The patterned OTS-SAM was immersed in an anhydrous toluene (99.8%, water < 0.002%, Aldrich) solution containing 0.1 M tantalum (V) ethoxide (Gelest Inc.) for 30 min in a N_2 atmosphere in a glove box. When the experiments were carried out in air, many particles homogeneously nucleated in the solution and they became attached to a deposited thin film. This observation firmly shows that elimination of traces of water is important to fabricate high quality thin films. The estimated partial pressure of H_2O in a N_2 atmosphere is below 0.1 hPa, while it was $\sim$15.8 hPa in air (estimated at 25 °C, relative humidity 50%). The ethoxy groups of the tantalum (V) ethoxide react with the H_2O changing into OH, which further reacts with the silanol groups of the SAM resulting in the formation of Ta–O–Si bonds (Fig. 1). The hydroxyl groups of the molecule are further condensed to form Ta–O–Ta bonds. The thickness of a film can be easily controlled by the soaking time because the condensation of tantalum (V) ethoxide progresses gradually in the solution. After having been immersed in the tantalum (V) ethoxide solution, the SAM substrate was rinsed with toluene and stored in air. The deposited thin films were not peeled off by sonication for 60 min, which shows their strong adhesion to the silanol group surfaces.

Site-selective deposition of thin films on the OTS-SAM was confirmed by SEM observation (Fig. 2). The films deposited in the silanol regions showed as black contrast in the SEM micrographs (Fig. 2b–d), while the silanol regions showed as white contrast in the SEM micrographs of a patterned OTS-SAM before immersion (Fig. 2a). This difference shows the predominant deposition of thin films on the silanol regions. The thickness of the film was less than 1 μm and it was hard to observe as shown in a tilted image of the micropattern (Fig. 2d). The image also shows many particles deposited on the whole substrate. These particles probably nucleated in the solution and adhered to the substrate. The homogeneous nucleation of the particles that is caused by high supersaturation of the solution should be reduced to obtain sharper micropatterns through selective-deposition via heterogeneous nucleation at the substrate surface.

The thickness of the films was evaluated using an atomic force microscope. The films obtained after soaking for 30 min were 52 nm thick. In addition, the thickness measured using an ellipsometer was 46 nm. The difference in the evaluated thickness is probably caused by the roughness of the film.

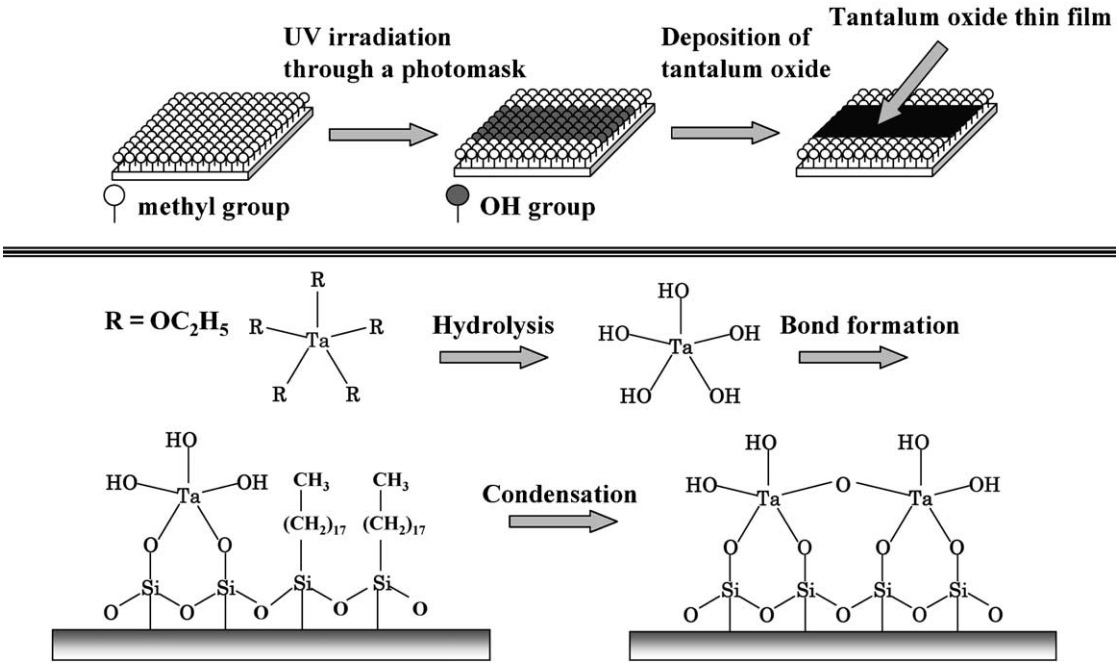

Fig. 1. Conceptual process for site-selective deposition of tantalum oxide thin film using a self-assembled monolayer.

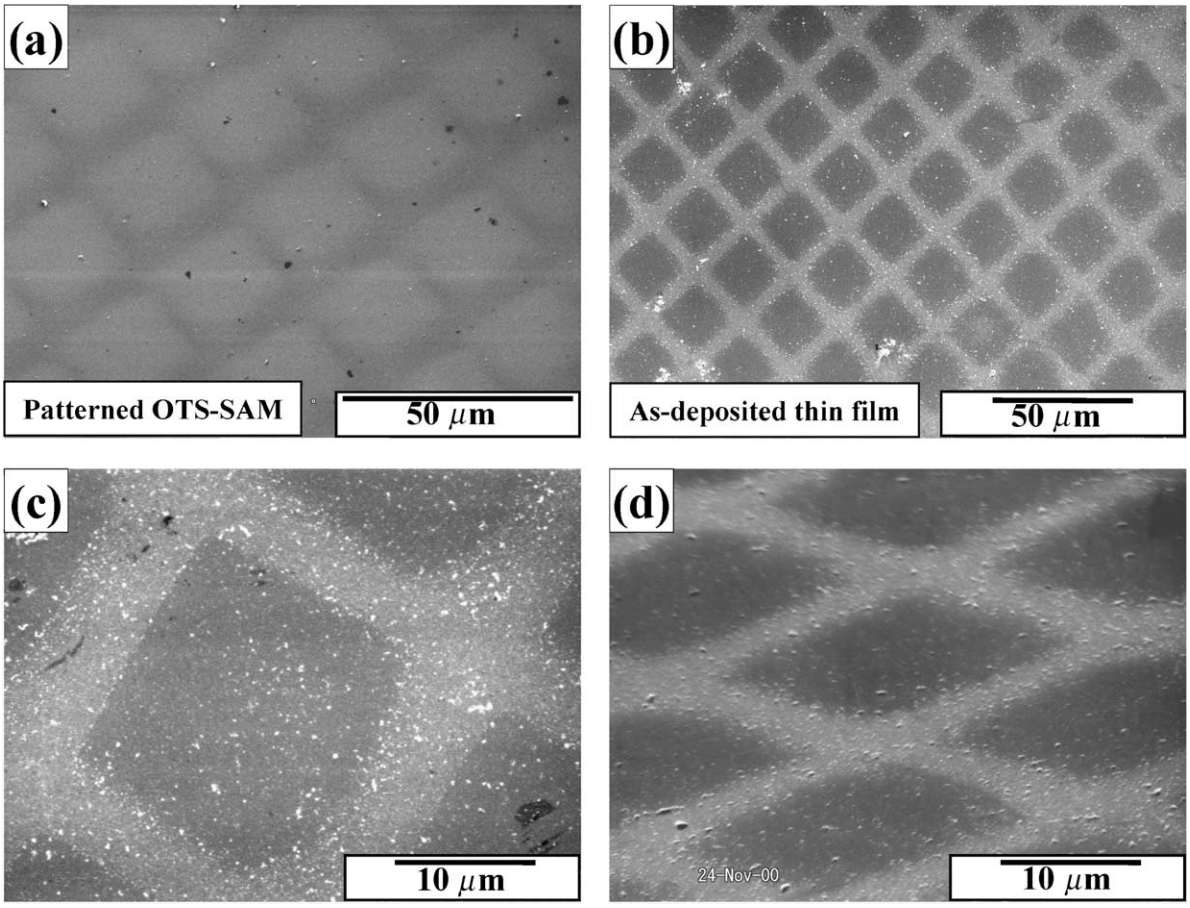

Fig. 2. SEM micrographs of (a) a patterned OTS-SAM and (b) a micropattern of as-deposited thin films, (c) magnified area of (b), and (d) tilted 75° image of (c).

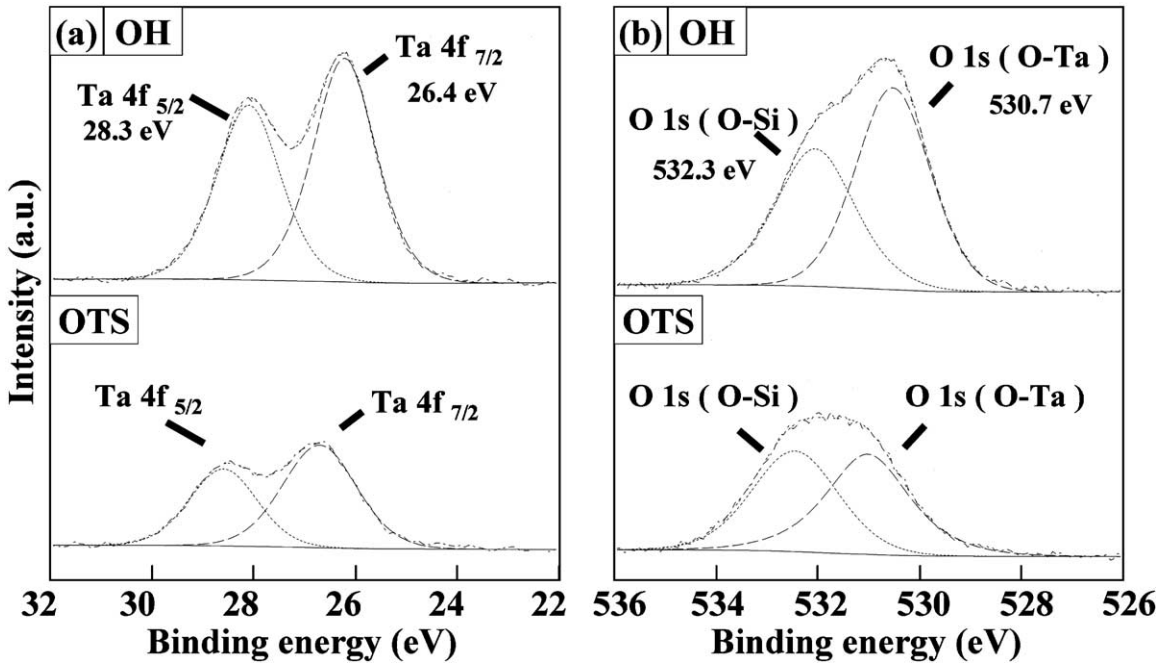

Fig. 3. XPS spectra of thin films formed on (a) silanol region or (b) octadecyl region of OTS-SAM.

3.2. Characterization of deposited $Ta_2O_5 \cdot 4H_2O$ thin films

The thin films were further evaluated using x-ray photoelectron spectroscopy. The spectral peaks corresponding to Ta $4f_{7/2}$ (26.4 eV) and Ta $4f_{5/2}$ (28.3 eV) were observed from thin films deposited on the silanol region (Fig. 3). This binding energy is higher than that of Ta metal (Ta $4f_{7/2}$: 21.6 eV,[23,24] 21.8 eV[25,26]) and similar to that of Ta_2O_5 (Ta $4f_{7/2}$: 26.5 eV,[23] 26.7 eV[24]). This suggests the tantalum atoms in thin films are positively charged relative to that of tantalum metal by formation of direct bonds with oxygen. On the other hand, the intensity of the Ta 7f spectrum detected from the octadecyl region was half of that from the silanol region. This suggests predominant deposition of thin films on the silanol regions.

An O 1s spectrum was observed from the silnaol regions and divided into O 1s (530.7 eV) and O 1s (532.3 eV). O 1s (532.3 eV) can be assigned to the silicon oxide layer on the surface of the silicon wafer (532.0eV[27]). The binding energy of O 1s (530.7 eV) is similar to that of Ta_2O_5 (530.9 eV[25]), and this suggests the presence of chemical bonds between oxygen atoms and tantalum atoms. The ratio of tantalum to oxygen was estimated from the Ta $4f_{7/2}$ (26.4 eV) spectrum and O 1s (530.7 eV) spectrum to be Ta:O = 1:4.13. This shows excessive oxygen atoms are contained in the thin films compared with Ta_2O_5.

The deposited films were evaluated using Fourier-transform infrared spectroscopy. A broad peak appearing at 610 cm^{-1} was assigned to Ta_2O_5 (Fig. 4), indicating a direct bond between tantalum atoms and oxygen atoms. Broad peaks were also observed at 3500 and 1630 cm^{-1}, and their intensities were decreased by annealing at 200–800 °C as shown in Fig. 4. These absorption bands can be ascribed to the vibration of the hydroxyl groups. The deposited film was considered to contain tantalum hydroxide and/or water molecules forming hydrated tantalum oxide.

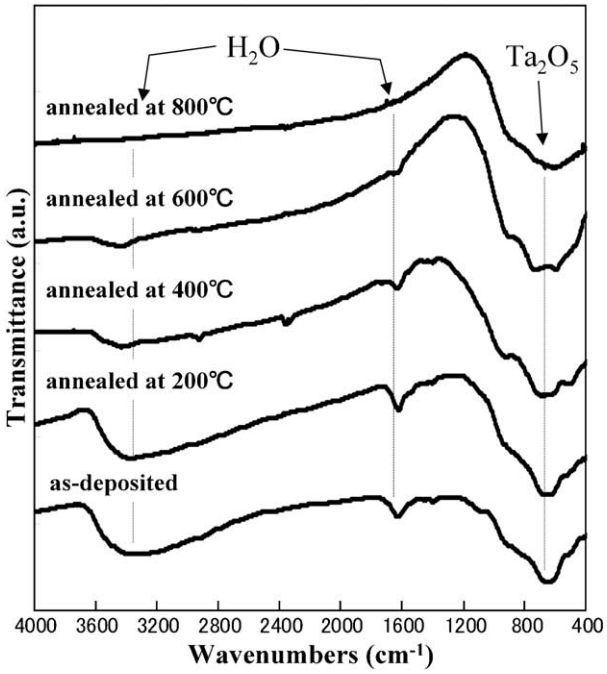

Fig. 4. IR spectra of as-deposited tantalum oxide thin film and those after annealing at different temperatures.

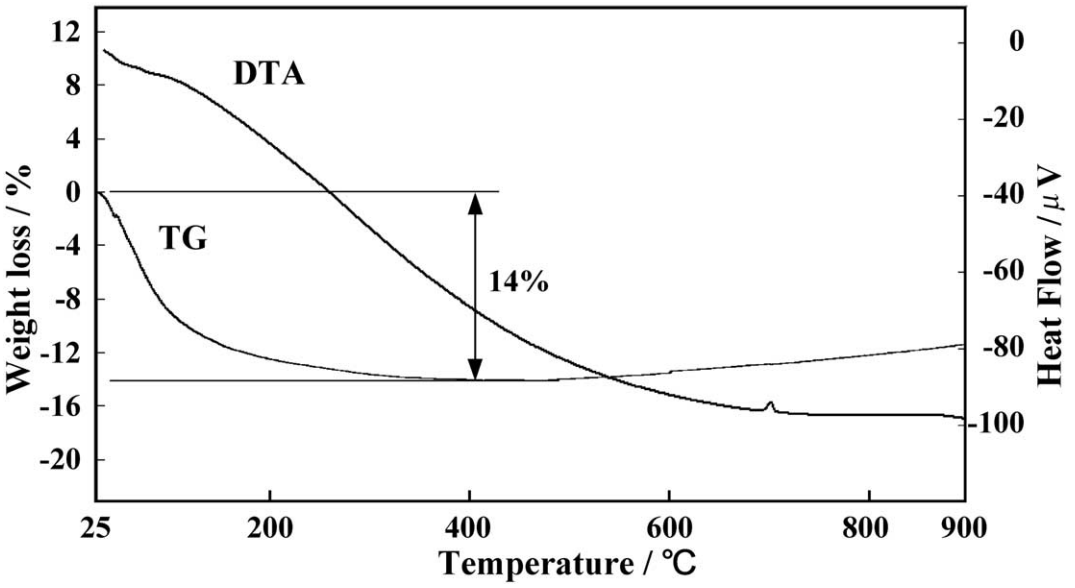

Fig. 5. TG-DTA curves for the collected precipitate.

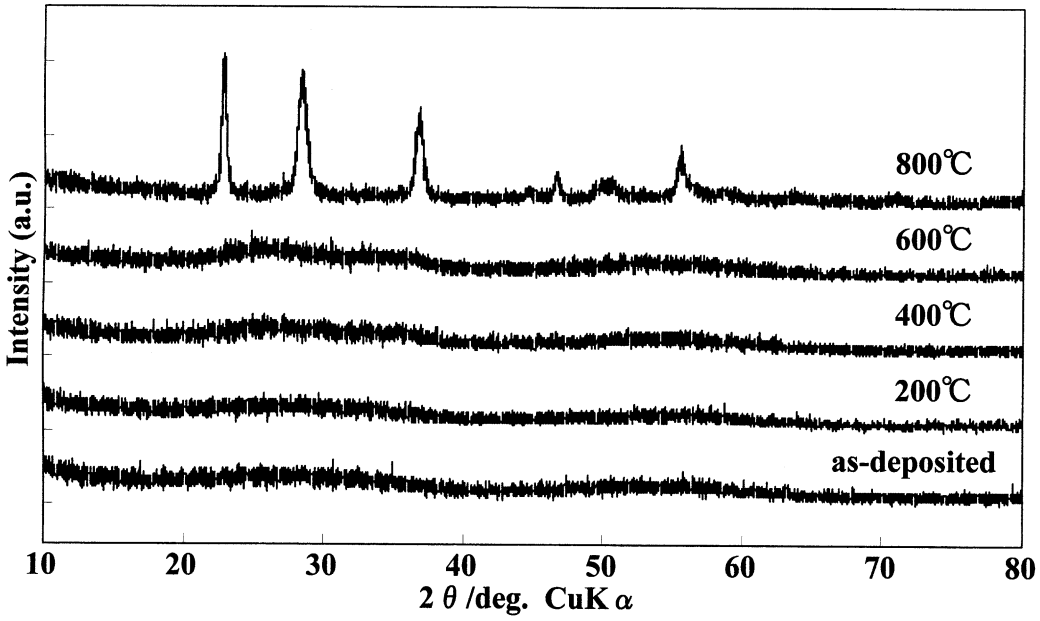

Fig. 6. XRD patterns of thin films changing with the change in annealing temperature.

Thermogravimetric analysis (TG) and differential thermal analysis (DTA) of the deposition were further conducted (Fig. 5). The total weight-loss in the temperature region up to 400 °C investigated through TG analysis was about 14 wt.% of the initial sample weight. This weight-loss was probably caused by the release of water molecules. The chemical composition of the as-deposited film was estimated using the concentration of water molecules (14 wt.%) assuming the chemical composition to be $Ta_2O_5{\cdot}nH_2O$ or $Ta_2O_{5-n}(OH)_{2n}$, which is expected from XPS and FT-IR measurements. The "n" in $Ta_2O_5{\cdot}nH_2O$ was calculated to be 3.99 and the deposition was expected to have a nominal composition of $Ta_2O_5{\cdot}4H_2O$ or $Ta_2O(OH)_8$.

3.3. Crystallization of $Ta_2O_5{\cdot}4H_2O$ to Ta_2O_5 and a micropattern of Ta_2O_5 thin films

Heat treatment of the films has demonstrated that the amorphous phase converts into crystalline orthorhombic Ta_2O_5 above 800 °C (Fig. 6). The crystallization started to occur between 600 and 800 °C. This agrees with an exothermic peak appearing at 700 °C in the DTA curve.

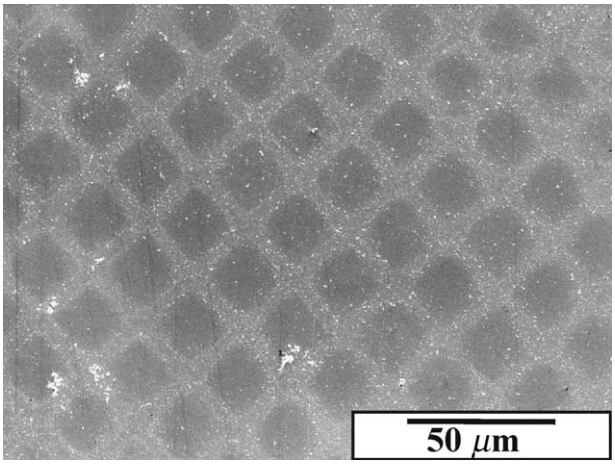

Fig. 7. SEM micrograph of a micropattern of thin films after annealing at 800 °C for 2 h.

A micropattern of crystalline Ta_2O_5 thin films obtained after heating at 800 °C for 2 h is shown in Fig. 7. No cracks were observed from the micrograph and the feature edge acuity of the pattern remained almost unchanged. This result suggests that micropattern of crystalline Ta_2O_5 thin films can be fabricated by our patterning and heat treatment process.

4. Conclusions

Patterned OTS-SAM was immersed in a tantalum (V) ethoxide solution to selectively deposit $Ta_2O_5{\cdot}4H_2O$ ($Ta_2O(OH)_8$) thin films on silanol groups regions. Site-selective deposition of thin films was realized and a micropattern was successfully fabricated at room temperature. Amorphous thin film of $Ta_2O_5{\cdot}4H_2O$ transformed into a crystalline Ta_2O_5 film after annealing at 800 °C for 2 h in air. The feature edge acuity of the micropattern remained unchanged by the annealing. This process can be applied to fabricate micropatterns of Ta_2O_5 thin films. However, adhesion of particles to the entire substrate should be suppressed and the feature edge acuity of the micropattern must be improved to make the patterns practical for future electronic devices.

References

1. Ishikawa, I. and Sugimoto, K., *Corros. Eng.*, 1989, **38**, 619.
2. Terui, H. and Kobayashi, M., Refractive-index-adjustable SiO_2–Ta_2O_5 films for integrated optical circuits. *Appl. Phys. Lett.*, 1978, **32**, 666–668.
3. Cava, R. F., Peck, W. F. Jr. and Krajewski, J. J., Enhancement of the dielectric constant of Ta_2O_5 through substitution with TiO_2. *Nature*, 1995, **377**, 215–217.
4. Kimura, S., Nishioka, Y., Shintani, A. and Mukai, K., Leakage-current increase in amorphous Ta_2O_5 films due to pinhole growth during annealing below 600 °C. *J. Electrochem. Soc.*, 1983, **130**, 2414–2418.
5. Nishioka, Y., Shinriki, H. and Mukai, K., Dielectric characteristics of double layer structure of extremely thin Ta_2O_5/SiO_2 on Si. *J. Electrochem. Soc.*, 1987, **134**, 410–415.
6. Clem, P. G., Jeon, N. L., Nuzzo, R. G. and Payne, D., Monolayer-mediated deposition of tantalum (V) oxide thin film structure from solution precursors A. *J. Am. Ceram. Soc.*, 1997, **80**(11), 2821–2827.
7. Masuda, Y., Sugiyama, T., Lin, H., Seo, W. S. and Koumoto, K., Selective deposition and micropatterning of titanium dioxide thin film on self-assembled monolayers. *Thin Solid Films*, 2001, **382**, 153–157.
8. Masuda, Y., Jinbo, Y., Yonezawa, T. and Koumoto, K., Templated site-selective deposition of titanium dioxide on self-assembled monolayers. *Chem. Mater.*, 2002, **14**(3), 1236–1241.
9. Masuda, Y., Seo, W. S. and Koumoto, K., Selective deposition and micropatterning of titanium dioxide on self-assembled monolayers from a gas phase. *Langmuir*, 2001, **17**(16), 4876–4880.
10. Masuda, Y., Seo, W. S. and Koumoto, K., Two-dimensional arrangement of fine silica spheres on self-assembled monolayers. *Thin Solid Films*, 2001, **382**, 183–189.
11. Masuda, Y., Seo, W. S. and Koumoto, K., Arrangement of nanosized ceramic particles on self-assembled monolayers. *Jpn. J. Appl. Phys*, 2000, **39**, 4596–4600.
12. Masuda, Y., Itoh, M., Yonezawa, T. and Koumoto, K., Low-dimensional arrangement of SiO_2 particles. *Langmuir*, 2002, **18**(10), 4155–4159.
13. Saito, N., Haneda, H., Sekiguchi, T., Ohashi, N., Sakagushi, I. and Koumoto, K., Low-temperature fabrication of light-emitting zinc oxide micropatterns using self-assembled monolayers. *Adv. Mater*, 2002, **14**(6), 418–421.
14. Zhu, P. X., Masuda, Y. and Koumoto, K., Site-selective adhesion of hydroxyapatite microparticles on charged surfaces in a supersaturated solution. *J. Colloid Interface Sci.*, 2001, **243**(1), 31–36.
15. Masuda, Y., Sugiyama, T. and Koumoto, K., Micropattening of anatase TiO_2 thin films from an aqueous solution by site-selective immersion method. *J. Mater. Chem.*, 2002, **12**(9), 2643–2647.
16. Masuda, Y., Wang, D. J., Seo, W. S. and Koumoto, K., Fabrication of micropatterned dielectric thin films on self-assembled monolayers. *Key Engineering Materials*, 2002, **214**, 157–162.
17. Wang, D. J., Masuda, Y., Seo, W. S. and Koumoto, K., Metal-oxide-semiconductor (mos) devices composed of biomimetically synthesized TiO_2 dielectric thin films. *Key Engineering Materials*, 2002, **214**, 163–170.
18. Ulman, A., *An Introduction to Ultrathin Organic Films from Langmuir-Blodgett to Self-Assembly*. Academic Press, New York, 1991 (and references therein).
19. Schrof, W., Rozouvan, S., Keuren, E. V., Horn, D., Schmitt, J. and Decher, G., Nonlinear optical properties of polyelectrolyte thin films containing gold nanoparticles investigated by wavelength dispersive femtosecond degenerate four wave mixing (DFWM). *Adv. Mater.*, 1998, **10**, 338–341.
20. Lin, W. B., Lin, W. P., Wong, G. K. and Marks, T. J., Supramolecular approaches to second-order nonlinear optical materials. Self-assembly and microstructural characterization of intrinsically acentric [(aminophenyl)azo]pyridinium superlattices. *J. Am. Chem. Soc.*, 1996, **118**, 8034–8042 (and references therein).
21. Roscoe, S. B., Kakkar, A. K., Marks, T. J., Malik, A., Durbin, M. K., Lin, W. P., Wong, G. K. and Dutta, P., Self-assembled chromophoric NLO-active monolayers. X-ray reflectivity and second-harmonic generation as complementary probes of building block-film microstructure relationships. *Langmuir*, 1996, **12**, 4218–4223.
22. Tillman, N., Ulman, A., Schildkraut, J. S. and Penner, T. L., Incorporation of phenoxy groups in self-assembled monolayers of trichlorosilane derivatives. Effects on film thickness, wettability, and molecular orientation. *J. Am. Chem. Soc.*, 1988, **110**, 6136–6144.

23. Wagner, C. D. *Practical Surface Analysis. 2nd edn.,* ed. D. Griggs and M. P. Seah. John Wiley, 1990, pp. 595.
24. Moulder, J. F., Stickle, W. F., Sobol, P. E. and Bomben, K. D. *Handbook of X-ray Photoelectron Spectroscopy. 2nd edm.,* ed. J., Chastain. Perkin-Elmer, 1992
25. Imai, Y., Watanabe, A., Mukaida, M., Osato, K., Tsunoda, T., Kameyama, T. and Fukuda, K., Stoichiometry of tantalum oxide films prepared by KrF excimer laser-induced chemical vapor deposition. *Thin Solid Films*, 1995, **261**, 76–82.
26. McGuire, G. E., Schweitzer, G. K. and Carlson, T. A., Core electron binding energies in some Group IIIA, VB, and VIB compounds. *Inorganic Chem*., 1973, **12**, 2450–2453.
27. Huang, D., Xiao, J.-H., Huang, Z-D., Gu, N.-P. and Yuan, C-W., TiO_2 thin films formation on industrial glass through self-assembly processing. *Thin Solid Films*, 1997, **305**, 110–115.