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Micropatterning of SnO_2 thin films using hydrophobic–hydrophilic patterned surface

Kiyoharu Tadanaga [a,*], Takayuki Fujii [a], Atsunori Matsuda [b], Tsutomu Minami [a], Masahiro Tatsumisago [a]

[a] *Department of Applied Materials Science, Graduate School of Engineering, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan*
[b] *Department of Materials Science, Toyohashi University of Technology, Toyohashi, Aichi 441-8580, Japan*

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Abstract

SnO_2 micropatterns were prepared by using hydrophobic–hydrophilic patterned surfaces. Hydrophobic–hydrophilic patterned surfaces were prepared by selective UV-irradiation through a photomask on multilayered films of a very thin TiO_2 gel layer and a hydrolyzed fluoroalkyltrimethoxysilane layer. SnO_2 precursor solution prepared from $SnCl_2$ and ethanol was coated on the hydrophobic–hydrophilic patterned surfaces. Convexly shaped SnO_2 patterns were formed on hydrophilic area of the patterned surfaces. Thickness of these patterns was more than 1 μm. This patterning technique must have a wide variety of applications such as fabrication of micro-optical components and micropatterned oxide thin films.

Keywords: Patterning; Hydrophobic–hydrophilic pattern; UV-irradiation; Surface tension

1. Introduction

Fine patterning techniques of sol–gel derived films have attracted much attention for the practical applications of these films to devices like integrated optical circuits and micro-electronic memories [1–9]. One approach to generate fine patterned oxide thin films is irradiation of UV light on photosensitive precursor gel films. Micropatterning of oxide thin films using patterned self-assembled monolayers has also been reported [10–12]. Very recently, we have proposed a new approach to form convexly shaped SiO_2 micropattern by using superhydrophobic–superhydrophilic patterned surface [13–15].

On the other hand, transparent, conductive SnO_2 thin films are widely used as sensors and transparent electrodes for various optoelectronic applications. Since SnO_2 has high chemical durability, patterning of SnO_2 thin films by chemical etching is very difficult, and thus Sn-doped In_2O_3 films have been used as finely patterned transparent electrodes so far. However, SnO_2 thin films have high optical transparency, high chemical durability, and a low cost for starting materials. SnO_2 thin films are thus very attractive for use in finely patterned transparent electrodes, if available. We have already reported the preparation of finely patterned transparent, conductive SnO_2 thin films through UV-irradiation on SnO_2 precursor films from $SnCl_2$ with acetyl acetone [6]. Shirahata et al. reported on the micropatterning of SnO_2 ultrathin films using a patterned self-assembled monolayer [12].

In this study, we have prepared SnO_2 micropatterns by using hydrophobic–hydrophilic patterned surfaces. Ethanol solution of $SnCl_2$ was used as the precursor solution, and convexly shaped micropatterns of SnO_2 were obtained by spin coating of the precursor solution.

2. Experimental

Hydrophobic–hydrophilic patterned surfaces were prepared on glass substrates by selective UV-irradiation through a photomask on double-layered films of a very thin TiO_2 gel film as the underlayer and a hydrolyzed fluoroalkyltrimethoxysilane (FAS) layer as the top layer. Very

* Corresponding author. Tel.: +81-72-254-9333; fax: +81-72-254-9913.
E-mail address: tadanaga@ams.osakafu-u.ac.jp (K. Tadanaga).

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thin TiO_2 gel layers of about 50 nm thick were formed using titanium n-butoxide, ethanol, acetyl acetone, and water. The TiO_2 gel layer was coated on non-alkali glass substrates and heat-treated at 500 °C. Heptadecafluorodecyltrimethoxysilane, which is one of the fluoroalkyltrimethoxysilanes (FAS), was used as a water repellent agent. UV light from a high-pressure mercury lamp (about 150 mW cm^{-2}) was irradiated on the films through a photomask for 15 min.

Precursor solutions were prepared by dissolving $SnCl_2$ in ethanol. The precursor solution was then spin-coated on the hydrophobic–hydrophilic micropattern and heat-treated in an electronic furnace. The morphology of the coating was examined using optical microscope and a surface profilometer.

3. Results and discussion

The two layered coating film which consists of a thin TiO_2 gel layer and a FAS layer showed hydrophobic property; the contact angles for water on these two layered films were about 110°. After UV light irradiation from a high-pressure mercury lamp, the contact angle for water on the two layered coating films became less than 5°. By irradiation of UV-light through a photomask on the hydrophobic surface, well-defined hydrophobic and hydrophilic regions were formed.

Fig. 1 shows the optical photograph of SnO_2 micropattern formed on the hydrophobic–hydrophilic patterned surface using the precursor solution from $SnCl_2$. The surface profile of the micropattern is also shown. The SnO_2 micropattern shown in Fig. 1 was prepared using a 50 mm mesh as a photomask, spin coating with 3000 rpm, and heat-treatment at 300 °C. The solution using $SnCl_2$ was coated only on the hydrophilic regions of the pattern, and convexly shaped SnO_2 micropatterns were formed without cracks after heat-treatment of 300 °C. In each pattern, the same number of interference fringes was observed, meaning that each pattern has the shape of a convex lens with almost the same shape and height. The height of the pattern in this study is about 1.0 mm. It was confirmed that these patterns were uncracked with heat-treatment up to 600 °C.

Fig. 2 shows the heat-treatment temperature dependence of average height of the pattern with spin speed of 1000, 3000 and 5000 rpm. When the spin speed for the deposition of precursor solution was 1000 rpm, the height of the pattern is about 2.0 mm, which is about two times larger than that of the pattern with 3000 and 5000 rpm. This indicates that the thickness of the pattern can be controlled by the spin speed as well as the concentration of the precursor solution. In each spin speed, the height of the pattern slightly decreases with an increase in the heat-treatment temperature. The X-ray diffraction measurements of these films showed that SnO_2 crystals with rutile structure were formed with the heat-treatment at 300 °C, and the crystallinity was increased with an increase in the heat-treatment temperature. These

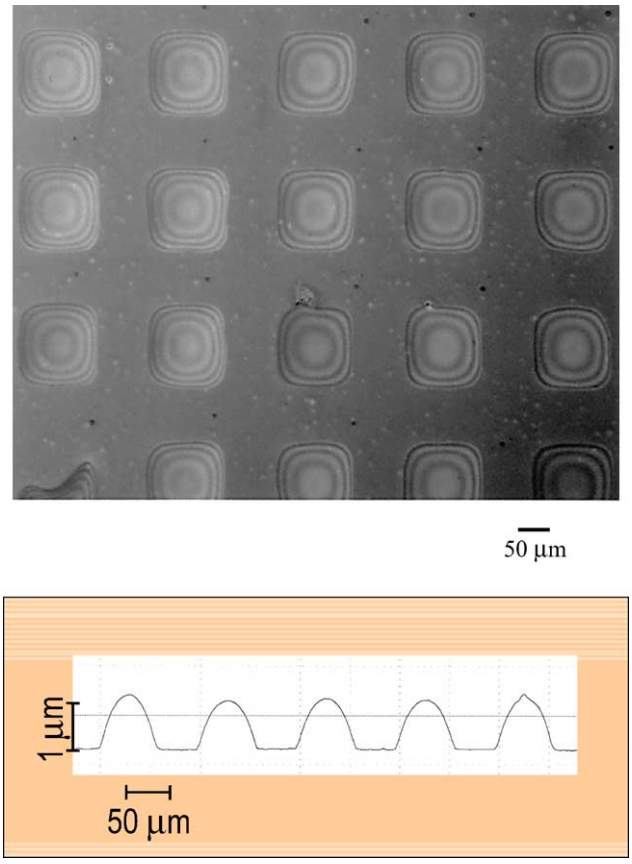

Fig. 1. Optical photograph of SnO_2 micropattern formed on the hydrophobic–hydrophilic patterned surface using the precursor solution from $SnCl_2$, and the surface profile of the micropattern.

results indicate that the SnO_2 thin films were not easily sintered with the heat-treatment.

It was confirmed that micropatterns were also formed in the films prepared using $ZrCl_4$, $AlCl_3$, and $TiCl_4$ [16]. Thus, this patterning technique potentially has a wide variety of applications such as fabrication of micro-optical components and finely patterned transparent electrodes.

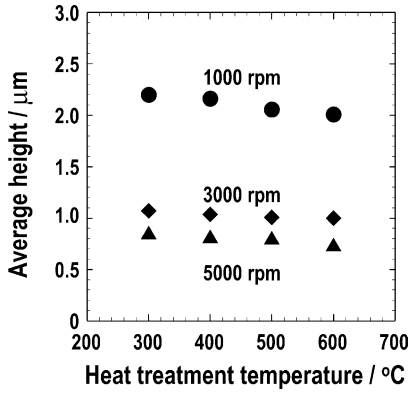

Fig. 2. Heat-treatment temperature dependence of average height of the pattern with spin speed of 1000, 3000 and 5000 rpm.

4. Conclusions

It was found that convexly shaped SnO_2 micropatterns were formed on the hydrophilic region of the pattern when $SnCl_2$ and ethanol was used as starting materials. This patterning technique must have a wide variety of applications such as fabrication of micro-optical components and finely patterned transparent electrodes.

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