

# Biomimetic Micropatterning of Titanium Dioxide Thin Films for Gate Dielectrics

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We have succeeded in fabricating micropatterns of TiO<sub>2</sub> thin films on self-assembled monolayers (SAMs). SAMs of OTS (octadecyltrichlorosilane) were formed on Si wafers and modified by UV irradiation using a photomask to generate octadecyl/silanol-pattern. They were used as templates to deposit TiO<sub>2</sub> thin films by the use of TDD (titanium dichloride diethoxide) dissolved in toluene. Amorphous films were selectively deposited on silanol regions. Line width variation of the pattern was improved to be well below the current electronics design rule, 5%. Dielectric constant of an as-deposited TiO<sub>2</sub> thin film, dielectric properties of TiO<sub>2</sub>/SiO<sub>2</sub>/Si interface and leakage current density were evaluated by measuring I-V and C-V characteristics of the MOS (metal-oxide-semiconductor) device. Rather low leakage current was observed under high electric fields and the TiO<sub>2</sub> thin film with the thickness ~18 nm showed dielectric constant of ~22 at 100 kHz, which is more than 5 times as large as that of a usual SiO<sub>2</sub> dielectric layer. However, the resistivity of the TiO<sub>2</sub> film was estimated to be not high enough and the dielectric constant depended on frequency, both of which are disadvantages for a gate dielectric.

**Key Words** : Biomimetic, Micropatterning, Titanium dioxide, Thin film, Gate oxide

## INTRODUCTION

Material synthesis needs to be controlled at nanometer length scale. They should be synthesized at low temperatures from the viewpoint of environmentally friendly processing, but high performance must be maintained as well. When we look at living creatures, we find that they produce inorganic materials for their own purpose at ambient temperature and pressure. The fundamental concept that they employ for material manufacture is "to synthesize suitable materials with required size and shape, and arrange them in the target regions at the right time, thus building 3D architecture". In order to carry out this processing they have optimized the process based on the cell activities commanded by genes. This process is the so-called biomineralization, and molecular recognition or templating at organic/inorganic interfaces is very effectively utilized to control nucleation and crystal growth events[1-3].

We have attempted to apply the basic principle of biomineralization to artificial material synthesis and morphology control. Among a variety of biomimetic synthetic processes, we have concentrated on the utilization of self-assembled monolayers (SAMs) as typical molecular assemblies for micropatterning of oxide thin films via low temperature liquid phase reactions[4-7].

Micropatterning technology employed for microelectronic devices is based on usual lithography and etching processes. We have tried to apply SAMs to this device processing to enable nano/micropatterning to be carried out biomimetically by means of controlling the solidification processes at organic/inorganic

interfaces. The process we have proposed is schematically shown in Figure 1. A SAM is first formed on a solid substrate, and then an energy beam, such as UV light, X-ray, electron beam, ion beam, etc. is irradiated onto the specific regions of the SAM surface to modify the chemical properties (functional groups) to obtain a patterned SAM. This patterned SAM is immersed in a solution, and oxide thin films are selectively deposited on either modified surface or unmodified surface giving rise to an oxide micropattern. The difference in chemical reactivity between the two functional groups is reflected to the difference in the ability of templating (molecular recognition), thus leading to the site-selective solidification and deposition.

We successfully fabricated micropatterned TiO<sub>2</sub> films on SAMs of phenyltrichlorosilane (PTCS) using a liquid phase deposition process involving precipitation from aqueous solutions containing TiF<sub>6</sub><sup>2-</sup> ions[4]. In this scheme, PTCS-SAMs were exposed to UV irradiation through a photomask to have a phenyl/silanol-pattern

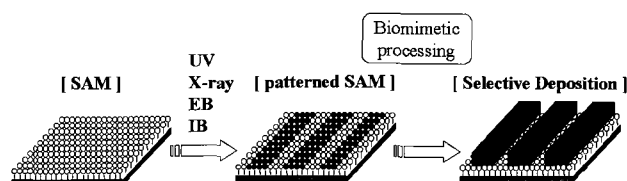


Figure 1 Biomimetic strategy for the fabrication of micropatterns.

and used them as templates.  $\text{TiO}_2$  (anatase) thin films were deposited on the whole area of SAM by means of a liquid phase deposition. While thin films on the phenyl region were easily peeled off by sonication, films on the silanol region were not removed, resulting in the formation of micropatterns of  $\text{TiO}_2$  (anatase). This process enables  $\text{TiO}_2$  (anatase) patterns to be formed on a large substrate without heating. However,  $\text{TiO}_2$  deposited on not only silanol regions but also on phenyl regions. It is necessary to deposit  $\text{TiO}_2$  on silanol regions selectively in order to realize patterns of higher resolution to be applied to microelectronic devices, such as gate oxide layers of metal-oxide-semiconductor field effect transistors (MOSFETs).

Here, we present a new process to realize site-selective deposition and generate high-resolution micropatterns of  $\text{TiO}_2$  thin films employing SAMs of octadecyl-trichlorosilane (OTS) and hydrolytic reactions of titanium alkoxide at room temperature. Thin films thus obtained showed dielectric properties suitable for the future gate oxide layers of MOSFETs[8].

## EXPERIMENTAL

P-type Si (100) wafers having the electrical resistivity of 4.5-6.0  $\Omega\text{cm}$  were employed for the substrates. They were cleaned ultrasonically in deionized water ( $>17.6\text{ M}\Omega\text{cm}$ ), immersed in a 1 : 1 (vol.)  $\text{HCl}/\text{CH}_3\text{OH}$  solution for 30 min, and cleaned again in deionized water. They were further immersed in conc.  $\text{H}_2\text{SO}_4$  for 30 min and then in boiling water for 5 min, and were cleaned with acetone. OTS-SAM was prepared by immersing the substrate into an anhydrous toluene (99.8%, water  $<0.002\%$ , Aldrich) solution containing 1 vol.% OTS (Aldrich) for 5 min under a  $\text{N}_2$  atmosphere. The substrate with SAM was then baked at  $120^\circ\text{C}$  for 5 min to remove residual solvent and to promote chemisorption of the SAM.

SAMs were exposed for 2 h to UV light (184.9 nm) from a Hg lamp (low-pressure mercury lamp) through a mesh for transmission electron microscope (TEM). The UV-irradiated regions become hydrophilic due to Si-OH group formation, while the nonirradiated region remained unchanged, i.e. it was composed of hydrophobic octadecyl groups, which gave rise to patterned OTS-SAM[9-12].

Patterned SAM substrates of OTS were immersed into an anhydrous toluene solution containing 0.1 M TDD (titanium dichloride diethoxide,  $\text{TiCl}_2(\text{OEt})_2$ ) for 5-30 min under a  $\text{N}_2$  atmosphere using a glove box. Micropatterns thus obtained were observed with an atomic force microscope (AFM), scanning electron microscope (SEM), and transmission electron microscope (TEM). They were further analyzed in terms of X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared spectroscopy (FT-IR).

To examine the dielectric properties of the MOS device composed of sputtered gold electrode,  $\text{TiO}_2$  thin film obtained by the present method, and p-type silicon semiconductor, current-voltage (I-V) characteristics and capacitance-voltage (C-V) characteristics were measured by connecting a source measure unit (Keithley 236) and an impedance analyzer (HP4192A), respectively.

## RESULTS AND DISCUSSION

### (1) Site-selective deposition and micropatterning of $\text{TiO}_2$

Micropattern of a thin film was successfully fabricated on

patterned OTS-SAM as shown in Figure 2. Thickness of films evaluated using AFM (Nanoscope E, Digital Instruments) was 6.9 nm and 27.4 nm for the soaking time of 5 min and 30 min, respectively. In the deposition process, chlorine atoms of TDD react with water molecules changing partially into molecules containing Ti-OH which further reacts with silanol groups of SAM resulting in the formation of Ti-O-Si bonds[13]. Actually, we observed FT-IR absorption band assigned to Ti-O-Si bonds. Ethoxy groups,  $-\text{O}-\text{C}_2\text{H}_5$ , of TDD are hydrolyzed into hydroxyl groups which are further condensed gradually to form Ti-O-Ti bonds[13]. Hydrolysis and condensation seem to take place cooperatively to form thin films of  $\text{TiO}_2$  only on the silanol surfaces, thus enabling the siteselective deposition. These films were not easily peeled off during sonication in acetone, and showed strong adhesion to the substrate.

Line width measurements at 15 equally spaced points on each line in Figure 2b indicate an average printed line width of  $23.3\mu\text{m}$ . Line edge roughness, as measured by the standard deviation of the line width, is  $\sim 0.5\mu\text{m}$ . This represents an  $\sim 2.1\%$  variation (i.e.  $0.5/23.3$ ) in the nominal line width. This variation is much better than that of the pattern fabricated with a liquid phase deposition process[4] and the usual 5% variation afforded by current electronics design rules. This variation is similar to that of a TEM mesh (2.1%) we used for Figure 2. Accordingly, the variation of the pattern can be improved by using a photomask of higher resolution.

Thin films were further evaluated by XPS (ESCALAB 210, VG Scientific,  $1\text{-}3\times 10^{-7}\text{ Pa}$ ). The X-ray source ( $\text{MgK}\alpha$ , 1253.6 eV) was operated at 15 kV and 18 mA. The spectral peak corresponding to Ti  $2p_{3/2}$  (458.5 eV) was observed from the thin film deposited on the silanol region (Figure 3). This binding energy is similar to that of  $\text{TiO}_2$  (458.4-458.7 eV)[14,15] and suggests the titanium atoms in the film are positively charged by formation of direct bonds with oxygen. In contrast, this spectrum was not observed from octadecyl regions also indicating the occurrence of site-selective deposition of the  $\text{TiO}_2$  films on silanol surfaces.

OTS-SAM surfaces showed O 1s (531.3 eV) which can be assigned to a silicon oxide layer on the surface of silicon wafer (532.0 eV[15])(Figure 4a). O 1s peak centered at 530.1 eV was observed from the thin films deposited on silanol regions (Figure 4b), and not observed from octadecyl regions. The intensity of this peak increased with soaking time (Figure 4c) and was not observed from octadecyl regions even after 30 min soaking. Hence, the peak (530.1 eV) was assigned to the deposited films. This binding energy is similar to that of  $\text{TiO}_2$  (529.9 eV[14], 530.1 eV[15]), and it indicated oxygen is negatively charged compared to neutral oxygen molecules (531.0 eV) possibly through the

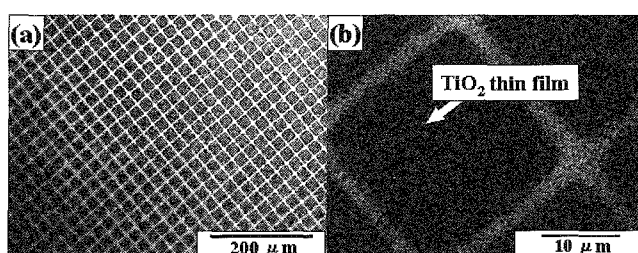


Figure 2 SEM photographs of (a) a micropattern of as-deposited thin films (30 min soaking); (b) magnified area of (a).

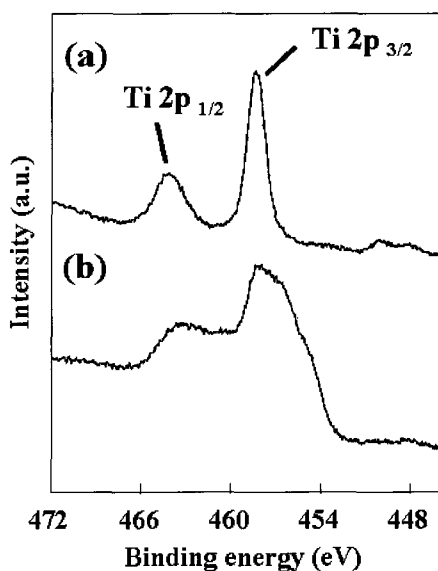


Figure 3 XPS spectra of Ti 2p for titanium oxide thin film formed on the silanol region of OTS-SAM (30 min soaking): (a) before and (b) after  $\text{Ar}^+$  sputtering.

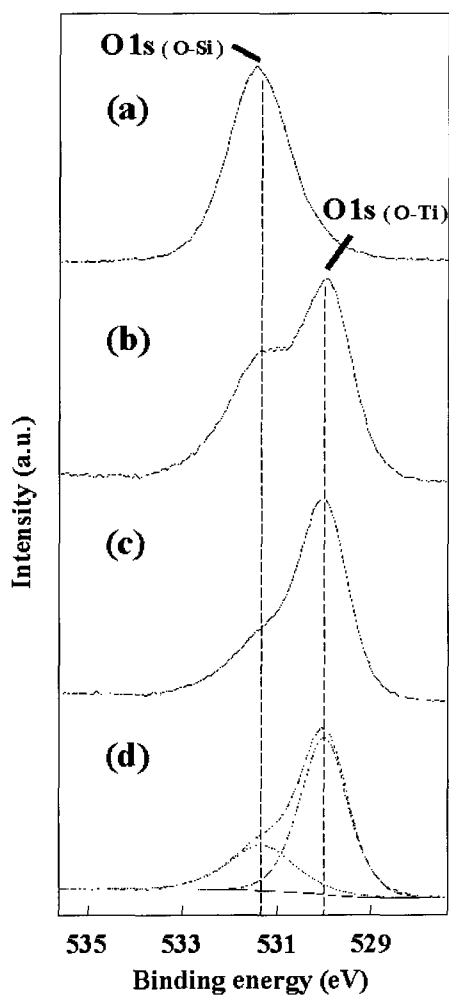


Figure 4 XPS spectra of O 1s: (a) octadecyl region of OTS-SAM; (b) thin film formed on the silanol region (5 min soaking); (c) thin film formed on the silanol region (30 min soaking); and (d) after  $\text{Ar}^+$  sputtering of (c).

formation of direct bonds with titanium.

The ratio of oxygen to titanium was evaluated after  $\text{Ar}^+$  ion sputtering for 20 min to avoid the influence of a contaminated layer on the surface (Figure 4d). O 1s peak can be deconvoluted into two curves [ratio of 529.7 eV (films) and 531.3 eV (silicon oxide) is 1 : 0.22]. The ratio of oxygen to titanium was estimated to be 2.2 : 1. Additionally, small amounts of chlorine and carbon were also detected ( $\text{Ti/O/Cl/C} = 1.0/2.2/0.17/0.37$ ), but the spectral peaks corresponding to C and Cl disappeared after annealing at 400°C.

## (2) Electrical properties of MOS devices

When the bias voltage is applied to the MOS device, normal high-frequency C-V characteristics is obtained as shown in Figure 5. The maximum constant capacitance of 102 nF is obtained at 100 kHz for the negative voltage. The MOS device consists of the series of  $\text{TiO}_2$  layer, native  $\text{SiO}_2$  layer, the space charge region near the Si surface and the bulk Si. When a large negative voltage is applied to the gate, the charges (holes) become accumulated in the semiconductor surface and the differential capacitance of the semiconductor becomes much larger than that of the dielectric oxide layers. Accordingly, the capacitance measured at negative bias voltage is simply the capacitance of the series of  $\text{TiO}_2$  layer and  $\text{SiO}_2$  layer. Based on the average thickness of a deposited  $\text{TiO}_2$  thin film (18.2 nm evaluated by AFM) and native  $\text{SiO}_2$  (2 nm), the dielectric constant of 21.6 at 100 kHz and 4.7 at 1 MHz for the  $\text{TiO}_2$  layer was estimated assuming the dielectric constant of  $\text{SiO}_2$  to be 3.9. The origin of the frequency dependence of dielectric constant is not well known, but it might be associated with the impurities (C and Cl) contained in the  $\text{TiO}_2$  film.

The change in the state of space charge region with the change

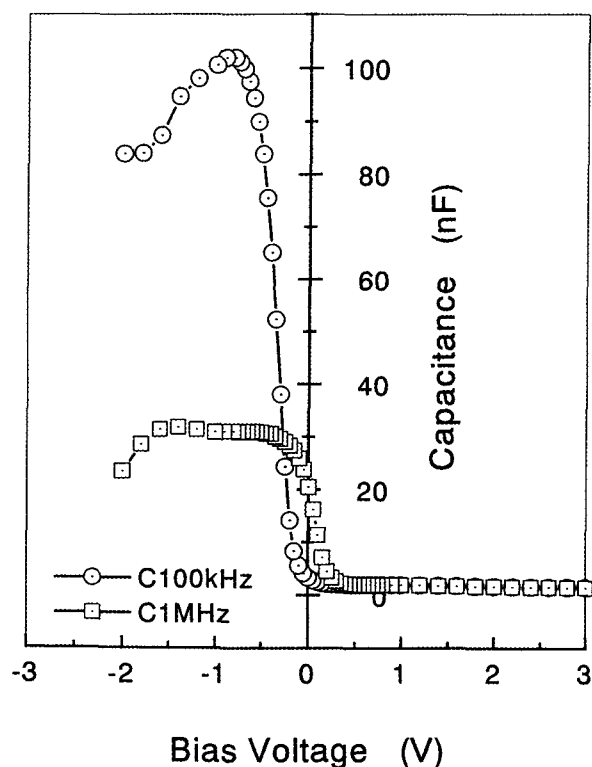


Figure 5 High-frequency C-V characteristics of the MOS device with  $\text{TiO}_2$  gate dielectric.

in bias voltage can be seen in the I-V characteristics of the TiO<sub>2</sub>/SiO<sub>2</sub>/p-Si MOS device (TiO<sub>2</sub>: 18.2 nm thick, SiO<sub>2</sub>: 2 nm thick) shown in Figure 6, which demonstrates asymmetric nonlinear resistance consistent with the rectification effect. Little current passes until the system breaks down at the voltage higher than 10.0 V which is not shown in the figure when reverse bias is applied (Au = positive, Si = negative), which is called OFF-state. However, when forward bias is applied, the device becomes ON-state and the current increases quickly with increasing voltage. Low leakage current density,  $1.3 \times 10^{-7}$  A/cm<sup>2</sup>, is observed below the voltage  $\sim 1.0$  V and resistivity of  $\sim 1.2 \times 10^{12}$  Ω cm is obtained for the TiO<sub>2</sub>/SiO<sub>2</sub> layer. Since the resistivity of SiO<sub>2</sub> is considered to be quite high, the present result would indicate that the resistivity of a TiO<sub>2</sub> layer is not high enough for a gate dielectric. Rather low resistivity of a TiO<sub>2</sub> layer might also be associated with the presence of impurities. We have attempted to obtain the TiO<sub>2</sub> film with higher purity and hence higher resistivity, by annealing in air at 100–300 °C, but unexpectedly the film became more conductive. XPS analysis did show the elimination of impurities by annealing. However, AFM observation of the annealed film indicated the grain growth taking place simultaneously forming pores (pin holes) which must have enhanced the leakage current leading to the appearance of low resistivity. Accordingly, thermal annealing is not effective to attain better quality of deposited TiO<sub>2</sub> film, and we can conclude that other more suitable starting materials and reaction systems should be exploited in the future study.

These observations indicate that the prepared MOS device possesses comparatively good capacitance and insulating characteristics. However, TiO<sub>2</sub> thin films synthesized biomimetically at room temperature still have some problems, such as large frequency dependence of dielectric constant and low

resistivity, and further improvement in the film quality ought to be achieved to realize the substitution for SiO<sub>2</sub> layers currently employed for gate dielectrics.

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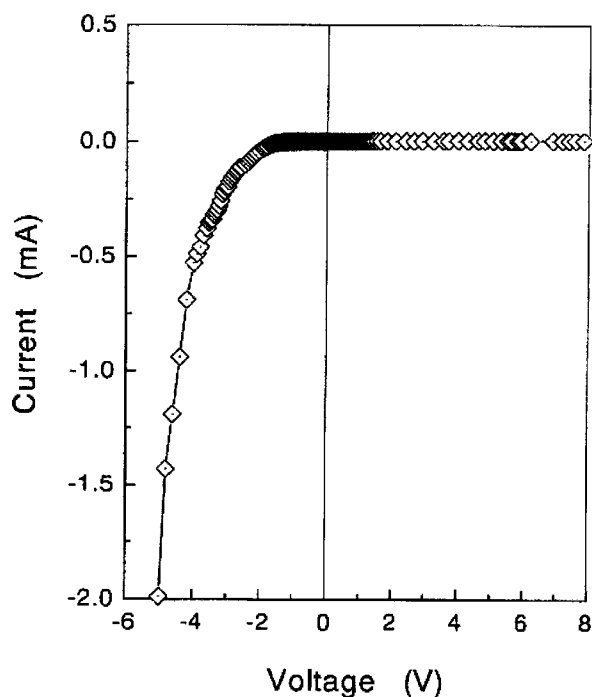


Figure 6 Current-voltage characteristics of the MOS device with TiO<sub>2</sub> gate dielectric.