Selective growth of TiO$_2$ thin films on Si(100) surfaces by combination of metalorganic chemical vapor deposition and microcontact printing methods


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We successfully patterned TiO$_2$ thin films by metalorganic chemical vapor deposition (MOCVD) on Si(100) substrates where the surface was first modified by an organic thin film. The organic thin film [octadecyltrichlorosilane (OTS)] of self-assembled monolayers (SAMs) was deposited by microcontact printing. Selective deposition of a 130 nm thick TiO$_2$ film was done on a 300–500 °C surface prepared by MOCVD without any carrier or bubbler gas. Auger electron spectroscopy and x-ray diffraction analyses showed that the deposited TiO$_2$ material was stoichiometric, polycrystalline, and consisted of anatase phase. Alpha-step profile and optical-microscopic images also showed that the boundaries between the OTS SAMs and selectively deposited TiO$_2$ thin film areas are definite and sharp. Capacitance–voltage measurement of a TiO$_2$ thin film yielded a dielectric constant of 29, suggesting possible application to electronic materials. © 2003 American Vacuum Society. [DOI: 10.1116/1.1585071]

I. INTRODUCTION

Oxide materials have a wealth of unique interesting physical properties that can be used for various technological applications.$^1$ Many oxide materials have been used extensively in the form of thin films because the applications involve microdevices that require materials fabricated on micron or submicron scales.$^{1,2}$ In recent years, titanium dioxide (TiO$_2$) films have found widespread application as materials for optical coatings and protective layers for large area integrated circuits because of their high refractive index and good insulating properties. Moreover, TiO$_2$ has a high dielectric constant of 180 along the c axis and 90 along the a axis, so it is useful in fabricating dielectric capacitors in micro-electronic devices. Bulk TiO$_2$ is known to have two main phases: rutile and anatase. Rutile is a high temperature stable phase and anatase is formed at lower temperatures. The structure of films strongly depends on the deposition temperature$^3$ and substrate surface properties.$^4$ Up to now TiO$_2$ has been extensively studied for its interesting electric,$^5,6$ magnetic,$^7$ catalytic,$^8$ and electrochemical properties.$^9$ Based upon these properties, a variety of technological applications of TiO$_2$ thin film are possible.

Various deposition techniques have been developed to deposit TiO$_2$ thin films, including evaporation, sputtering,$^{10}$ thermal oxidation of titanium and the chemical vapor deposition (CVD) method.$^{11}$ Among them, the CVD technique, which uses a metalorganic compound as a precursor (MOCVD), has many advantages, such as good conformal coverage, the possibility of epitaxial growth and selective deposition and application to large area deposition. This method is also one of low cost, and it is easy to control the deposition growth parameters. Thus, the MOCVD method is known to be one of the most powerful techniques and is suitable for stoichiometric and microstructure thin film deposition.$^{12}$

The patterning of thin films is of considerable scientific and technological interest. Various ways to obtain micro/nanopatterns of TiO$_2$ thin films have been thoroughly investigated.$^{13,14}$ In particular, microcontact printing ($\mu$CP) is a very convenient, nonphotolithographic technique that can generate patterned features of self-assembled monolayers (SAMs) on both planar and nonplanar surfaces.$^{15–18}$ The ability to control the wettability of a solid surface is tremendously important and useful in a range of technological applications. In addition, the microcontact printing technique shows that hydrophobic patterns with micron dimensions can be formed on hydrophilic surfaces without involving photolithographic-type procedures.$^{19}$

In this article we discuss the selective growth of TiO$_2$ thin films using MOCVD on Si(100) substrates$^{20,23}$ patterned by octadecyltrichlorosilane (OTS) applied by microcontact printing.

II. EXPERIMENT

First, the polydimethylsiloxane \( \{[-\text{Si(CH$_3$)$_2$O}]_n \} \) (PDMS) stamps used for microcontact printing octadecyltrichlorosilane \( \text{[CH$_3$(CH$_2$)$_{17}$SiCl$_3$]} \) (OTS), SAMs were fabricated according to a previously reported procedure.$^{18}$ A solution of OTS in dry hexane was used as the “ink.” The OTS solution was applied to the PDMS stamp using a spinner. Second, the stamp was brought into contact with the Si(100) substrates by hand and held in place for 30 s. After printing, TiO$_2$ thin films were deposited on these Si(100) substrates by MOCVD using titanium(iv) isoproxide \( \{\text{[Ti(O(C$_3$H$_7$)$_4]}\} \) (TIP) as a single molecular precursor. The patterned Si(100) substrate was pretreated with ethanol and de-ionized (DI) water in an ultrasonic cleaner without acid treatment to protect the patterning from being destroyed. The CVD experi-
ments were performed in a homemade MOCVD system. The MOCVD apparatus was fabricated using a quartz tube and stainless steel bodies connected through O-ring joints. Since TIP is very volatile at low temperature and contamination from it is small,\textsuperscript{22,23} it is not necessary to use any carrier or reactive gas to increase mass transportation or to remove contaminants in the film. The base pressure of the MOCVD apparatus was $1.0 \times 10^{-3}$ Torr, and the working pressure was kept in the range of $3.0 \times 10^{-2} - 4.0 \times 10^{-2}$ Torr. The deposition temperature was 300–500 °C, and the deposition was 0.5–2 h. Details of the experimental setup and deposition procedures were already published.\textsuperscript{20}

The as-grown films were characterized by x-ray diffraction (XRD) and their atomic composition using Auger electron spectroscopy (AES), optical microscopy (OM), alpha-step profiling, and capacitance–voltage ($C–V$) measurements.

### III. RESULTS AND DISCUSSION

Figure 1(a) shows XRD patterns of deposited TiO$_2$ thin films on the OTS patterned Si(100) substrates at 350 and 400 °C. The XRD patterns display characteristic peaks of anatase TiO$_2$ at $2\theta=25.0^\circ$, 48.0$^\circ$, and 55.0$^\circ$, which are attributed to diffraction of anatase TiO$_2$(101), (200), and (211) planes, respectively. Peaks of rutile phases were not observed. This is in good agreement with a previous result.\textsuperscript{20} Increasing the substrate temperature increased the intensities of the XRD peaks, suggesting that higher quality TiO$_2$ thin film can be obtained at higher temperatures. Similar results were also obtained on clean Si(100) substrates below 550 °C.\textsuperscript{20} XRD analysis showed that selectively deposited TiO$_2$ thin film has a polycrystalline anatase phase.

Figure 1(b) shows an optical microscopy image of the deposited TiO$_2$ thin film that was selectively grown on the OTS patterned Si(100) surface at 350 °C. Based on the AES analysis, the dark part of the image is the TiO$_2$ deposited area and the bright part of the image indicates the OTS SAM area. The selectivity of the deposition is more obvious from the AES shown in Fig. 2. The selectively TiO$_2$ deposited area in Fig. 2(a) shows only peaks of Ti, O and Ar, and the OTS SAM area in Fig. 2(b) hardly shows Ti and O peaks. With peak-to-peak intensity analysis, the film composition was determined for the TiO$_2$ deposited area and the OTS SAM area, respectively.

Table I shows the results of film composition analysis. The composition ratio between Ti and O shows approximately 1:2, indicating that stoichiometric TiO$_2$ thin film was selectively deposited on the Si(100) surface. However, in the OTS SAM area, only a very small amount of Ti was found.
This means that the reason for the large amounts of O, C, and Si is mainly due to the OTS rather than TiO$_2$ thin film formation, supporting the selective growth of TiO$_2$ thin films on the bare Si$_{100}$ surface. Therefore, Fig. 2 suggests that the TiO$_2$ only exists on the bare Si$_{100}$ surface and not in the OTS SAM area.

This result can be explained as follows. The terminal group of OTS (-CH$_3$) is hydrophobic, but TiO$_2$ thin films are hydrophilic. So TiO$_2$ thin films react only with hydrophilic materials such as SiO$_2$ and SiOH layers on Si$_{100}$ surfaces. Therefore, TiO$_2$ thin films were not deposited in the OTS SAM area, only on the Si$_{100}$ surface. From AES analysis, we found the deposited thin films were very stoichiometric TiO$_2$ film and we confirmed selective growth of TiO$_2$ thin film on the OTS patterned Si$_{100}$ surface.

Selectively deposited TiO$_2$ thin films can be identified directly by optical microscopy as shown in Fig. 3(a). The boundaries between the OTS SAM area and TiO$_2$ deposited area are very clean cut and sharp with no breaks. From our experiment, we conclude that microcontact printing is a very good easy method to use for patterning OTS SAMs on Si$_{100}$ substrates. The growth of TiO$_2$ thin films was selectively carried out even below 10 μm linewidth of OTS SAMs. This method of selective CVD on those surfaces may be useful in microelectronics processing.

Alpha-step profiling [Fig. 3(b)] was also performed on the patterned area shown in the optical image in Fig. 3(a) to analyze the surface morphology of the patterned TiO$_2$ lines. The thickness of the deposited TiO$_2$ thin film was measured as about 1300 Å, and the interface of deposited regions showed a nearly vertical shape, indicating that TiO$_2$ was deposited on bare Si$_{100}$ substrate regions selectively.

Figure 4(a) shows typical data of an AES depth profile for the selectively deposited TiO$_2$ thin film obtained by Ar ion sputtering on the TiO$_2$ deposited area in Fig. 1(b). From the AES depth profile data the stoichiometry of TiO$_2$ thin film is found to be Ti:O=1:2. The changes in surface atomic com-

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<th>Table 1. Atomic percent of Ti and O for selectively TiO$_2$ deposited areas and OTS SAM areas.</th>
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<td>Element</td>
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<tr>
<td>-----------------</td>
</tr>
<tr>
<td>Ti</td>
</tr>
<tr>
<td>O</td>
</tr>
<tr>
<td>C</td>
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<tr>
<td>Si</td>
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Fig. 3. Optical microscopic images and alpha-step profile data of selectively deposited TiO$_2$ thin films and SAM areas.

Fig. 4. (a) Depth profile of selectively deposited TiO$_2$ thin film shown in the dark area in Fig. 1(b). (b) Capacitance–voltage curve of the deposited TiO$_2$ thin film.

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position determined by Auger peak-to-peak analysis during depth profiling for the TiO2 deposited area in Fig. 1(b) are also given in Table II. The atomic compositions of Ti and O in the thin film show nearly a 1:2 ratio in the depth, which is in good agreement with the stoichiometry value of the bulk TiO2. Contamination from the precursor and diffusion of C and Si atoms between the TiO2 layer and OTS SAM layer almost never occur during CVD.

To determine the dielectric constant of TiO2 thin films, high frequency (1 MHz) C–V characteristics of Al/TiO2 film/p–Si metal–insulator–semiconductor (MIS) diode structures were measured at room temperature. The thickness of the TiO2 film used in the C–V measurement was about 2700 Å, and the area of the Al electrode was 0.332×10^{-6} m^2. Figure 4(b) shows the C–V curve of the TiO2 film deposited at 350 °C. A hysteresis loop was observed in the C–V curve shown in Fig. 4(b). The clockwise type hysteresis loop is a result of mobile charge, which is due primarily to ionic impurities. Accumulated charge on the TiO2 thin film surface occurs at −2.5 V, and inversion was also observed at positive bias. The surface accumulation capacitance was measured to be about 320 pF, which leads to a dielectric constant of 29 for the TiO2 film. The reasonably high dielectric constant suggests possible device applications of the films.

IV. CONCLUSIONS

Selective growth of TiO2 thin films was successfully carried out on a patterned Si(100) surface by a combination of metalorganic chemical vapor deposition and microcontact printing at deposition temperatures in the range of 300–500 °C. AES and XRD data showed the selectively deposited TiO2 has a stoichiometric composition in the depth and a polycrystalline anatase phase. Also, the boundaries between the OTS SAM area and the selectively TiO2 deposited area were very definite and sharp. From C–V measurements of the Al/TiO2/p–Si structure, the dielectric constant was calculated to be approximately 29 for the TiO2 thin films, suggesting the possibility of electronic materials applications.

ACKNOWLEDGMENTS

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Table II. AES depth profile quantification data obtained from the TiO2 deposited area in Fig. 1(b).

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<tr>
<th>Element</th>
<th>Surface (%)</th>
<th>After 20 s etching (%)</th>
<th>After 700 s etching (%)</th>
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<tr>
<td>Ti</td>
<td>31.7</td>
<td>34.1</td>
<td>4.4</td>
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<tr>
<td>O</td>
<td>63.5</td>
<td>61.7</td>
<td>1.7</td>
</tr>
<tr>
<td>C</td>
<td>1.4</td>
<td>1.6</td>
<td>3.3</td>
</tr>
<tr>
<td>Si</td>
<td>3.4</td>
<td>2.6</td>
<td>90.3</td>
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