Selective deposition of metal oxide thin films on Si(100) surfaces by combination of metal-organic chemical vapour deposition and microcontact printing methods

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Abstract
TiO$_2$, ZrO$_2$ and HfO$_2$ thin films have been deposited selectively using metal-organic chemical vapour deposition (MOCVD) technique with various single molecular precursors on Si(100) substrates which were patterned with octadecyltrichlorosilane (OTS) applied by microcontact printing ($\mu$CP). Titanium (IV) isopropoxide [Ti(O\textsubscript{i}Pr)$_4$], bis-isoproxy-bis-tertiarybutyl-acetoacetate zirconium [Zr(O\textsubscript{i}Pr)$_2$(tbaoac)$_2$] and hafnium tert-butoxide [Hf(O\textsubscript{t}Bu)$_4$] were used for titanium dioxide (TiO$_2$), hafnium and zirconium oxide (ZrO$_2$ and HfO$_2$) thin films, respectively. Selective depositions were successfully carried out in a home-made MOCVD system. All the deposited thin films had higher reactivity on bare silicon surfaces than OTS self-assembled monolayers (SAMs) deposited area. However, there was slightly different selective growth tendency on OTS deposited Si(100) surfaces. The selectivity tendency of the deposited thin films was revealed in order of TiO$_2$, HfO$_2$ and ZrO$_2$. This tendency was explained by means of film growth rate, structures and molecular weight of precursors and acidity of transition metal of precursors.

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(Some figures in this article are in colour only in the electronic version.)

1. Introduction

Soft lithography is a method to make micro/nano size patterns and structures simply using organic materials without involving high energy. In particular, microcontact printing ($\mu$CP) is a very convenient and nonphotolithographic technique that can generate patterned features of self-assembled monolayers (SAMs) on both planar and nonplanar surfaces. The ability to control the wettability of a solid surface is tremendously important and useful in a range of technological applications [1–3]. Oxide materials have a wealth of unique interesting physical properties that can be used for various technological applications. Many oxide materials have been used extensively in the form of thin films because the applications involve micro-devices that require materials fabricated on micron or submicron scales [4, 5]. Titanium dioxide (TiO$_2$) films have found widespread application as materials for optical coatings and protective layers for very large-scale integrated circuits because of their wide energy bandgap (3.2 eV), high refractive index (rutile: 2.7, anatase: 2.5), 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 [6–9]. Hafnium and zirconium oxide (HfO$_2$ and ZrO$_2$) have been extensively studied for use as a silicon dioxide (SiO$_2$) replacement in a gate-oxide insulating layer in complementary
metal oxide semiconductor (CMOS) devices because of their high dielectric constants (~25–30) and high bandgap energies (5.7–5.8 eV) [10]. These properties endowed upon ZrO$_2$ and HfO$_2$ which make them leading candidates for a gate-oxide replacement also give them high potential for application as an insulating dielectric in the capacitive element in many memory devices such as dynamic random access memory (DRAM). As these good properties and applications, metal oxide thin films have been deposited by several physical and chemical deposition techniques. Among them, chemical vapour deposition (CVD) technique using metal-organic compounds as a precursor has many advantages, such as good conformal coverage, the possibility of epitaxial growth and selective deposition and large area deposition. Thus metal-organic CVD (MOCVD) is well known as one of the most powerful techniques and is suitable for stoichiometric and micro-structured thin film deposition. In this paper, the selective growth of metal oxide thin films such as TiO$_2$, ZrO$_2$ and HfO$_2$ which can be formed on hydrophilic surfaces. The aim of the work is to fabricate metal oxide thin films with micro size and characterization of their growth behaviour and of their surface characterization.

2. Experimental

To make micro-size patterns on Si(100) substrates, polydimethylsiloxane (−[Si(CH$_3$)$_2$O]$_n$−, PDMS) elastomer stamp which has micro-size patterns was firstly fabricated according to a previously reported procedure [1]. A solution of OTS in dry hexane was used as the ink for pattern transfer from PDMS stamp to the Si(100) surfaces. Because the surface of the Si(100) is hydrophilic in nature and the terminal group of OTS has hydrophobic character, it was able to make hydrophobic area with micro-dimension on the Si(100) surface using OTS solution. Also OTS can easily form SAMs on the substrate. The OTS solution was deposited on the PDMS stamp using a spinner. After that, the PDMS stamp was brought into contact with the Si(100) surfaces by hand and held in place for 30 s. The OTS SAMs formed on the Si(100) surface can endure over 450 °C under 10$^{-3}$ Torr vacuum condition because they can make strong chemisorption with Si(100) surface. Various patterns were fabricated on Si(100) surfaces. Figure 1 shows a typical scanning electron microscopy (SEM) image of the substrate which was patterned by OTS SAMs using μCP. Patterned SAMs with different functional regions show image contrast due to the difference in the lowest unoccupied molecular orbital [11]. The dark strip regions are bare Si surfaces which have hydrophilic character, while the bright areas are OTS SAMs surfaces with hydrophobic character. To confirm the change of the surface property, contact-angle of the modified Si(100) surface as well as the bare Si(100) surface was measured. The contact-angle was about 32° on the bare Si(100) surface and about 112° on the OTS SAMs region, respectively. It means that the bare Si(100) surface has hydrophilic character and OTS patterned region has hydrophobic character. The OTS patterned Si(100) substrate was cleaned with ethanol and water in a ultrasonic cleaner for 5 min for metal oxide thin film deposition on them.

Thin film depositions were performed using a homemade CVD system fabricated using a quartz tube and stainless steel bodies connected through O-ring joints. It was evacuated using a mechanical pump. A graphite block was used as a heater which was controlled by a direct current power through Super–Kanthal wire inserted in it. A substrate can be mounted on the graphite heater. To get uniform thin films, it was located at a tilt in the centre of the reactor body. The substrate temperature was monitored by a K-type thermocouple. Metal oxide (TiO$_2$, ZrO$_2$ and HfO$_2$) thin films were deposited on the OTS printed Si(100) substrates by MOCVD using various metal-organic precursors. Titanium isopropoxide Ti(OPr)$_4$ [12], bis-isoproxy-bis-tertiarybutyl-acetoacetate zirconium [Zr(OPr)$_2$(tboaoc)$_2$] [13, 14] and hafnium tert-butoxide [Hf(O(Bu)$_4$)] were used for TiO$_2$, ZrO$_2$ and HfO$_2$ thin film depositions, respectively. Table 1 shows the deposition conditions. To study their growth behaviour, growth rates and possibility of selective growth on Si(100) surfaces,

| Table 1. Deposition conditions for TiO$_2$, ZrO$_2$, and HfO$_2$ thin films. |
|---------------------------------|-----------------|----------------|----------------|
| **Pre-cursor**                  | **Ti(OPr)$_4$** | **Zr(OPr)$_2$(tboaoc)$_2$** | **Hf(O(Bu)$_4$** |
| **Deposition pressure (Torr)**  | 3.0 × 10$^{-2}$ | 7.0 × 10$^{-2}$ | 3.0 × 10$^{-2}$ |
| **Deposition temperature (°C)**| 300–500         | 450–550         | 150–400         |
| **Deposition time (h)**         | 0.5–2.0         | 2.0–5.0         | 1.0             |
| **Carrier gas**                 | None            | N$_2$ gas (5 sccm) | None            |
| **Reaction gas**                | None            | None            | None            |

Figure 1. Typical SEM image of the Si(100) surfaces which were patterned by OTS SAMs using μCP method.
the as-grown films were characterized by optical microscopy (OM), SEM and atomic force microscopy (AFM).

3. Results and discussion

The metal oxide thin films deposited from various kinds of metal-organic precursors showed good area-selectivity on OTS patterned Si(100) surfaces. All the deposited thin films had higher reactivity on bare silicon surfaces than OTS SAMs deposited area. It means that the thin films prefer making depositions on the bare Si(100) surface to growing on OTS SAMs. However, there was slightly different selective growth tendency on OTS deposited Si(100) surfaces.

Figure 2 shows the OM image of TiO$_2$ thin film which was deposited on the OTS patterned Si(100) surface at 350 °C for 0.5 h. It shows a very clear OM image. The relatively dark part in this image is the TiO$_2$ deposited area and bright area is the OTS SAMs area. In the case of ZrO$_2$ and HfO$_2$ thin films, we can also confirm the boundary between film deposition area and OTS SAMs area, but it was not as clear as that of TiO$_2$ thin films. To make certain of selective growth and surface morphology of deposited thin films, SEM analyses were carried out subsequently. Figure 3(a) shows the deposited TiO$_2$ thin films at 350 °C for 0.5 h, and figure 3(b) shows the deposited ZrO$_2$ thin films at 450 °C for 2 h. For figure 3(a), very sharp and clear boundaries between TiO$_2$ deposited area and OTS SAMs area can be seen, and there were no trace of TiO$_2$ deposition on the OTS SAMs surface. In the case of ZrO$_2$ thin film, the selective deposition was carried out on the OTS patterned Si(100) surface, but the boundary shape was not clear enough and there was much evidence of ZrO$_2$ thin films growing on the OTS SAMs area. Such a phenomenon appeared in the case of HfO$_2$ deposition [15]. Figure 4 shows AFM images of selectively deposited TiO$_2$ thin films on OTS patterned Si(100) substrate at 350 °C for 0.5 h. The thickness of it was about 80 nm and it appeared good selectivity in the range of 3 μm. TiO$_2$ thin films showed very good selectivity, but deposited ZrO$_2$ and HfO$_2$ thin films showed relatively not such good selectivity compared to the TiO$_2$ thin films.

To confirm the difference in selectivity, the growth rates on to Si(100) substrates were studied. For this study, TiO$_2$, ZrO$_2$ and HfO$_2$ thin films were deposited on bare Si(100) substrates at various deposition temperatures. As-deposited metal oxide thin films were first analysed by means of SEM. Figure 5 shows SEM images of TiO$_2$, ZrO$_2$ and HfO$_2$ thin films grown by Ti(O'Pr)$_4$, Zr(O'Pr)$_2$(tbaoc)$_2$ and [Hf(O'Bu)$_4$] on Si(100) substrates at various deposition conditions, respectively. It was possible to deposit TiO$_2$ thin films on the substrate at 300 °C, and it showed rapid growth rate on the substrate. Because of the rapid growth rate, TiO$_2$ thin films were able to grow and made big grains on their surfaces as shown in figures 5(a) and (b). On the other hand, ZrO$_2$ thin films were able to deposit on the substrates over 400 °C with very slow growth rate and HfO$_2$ thin films were deposited on the substrates as low as 150 °C with very smooth surface morphologies. The film growth rate is calculated by the changes of film thickness that were measured by cross-sectional SEM images and alpha-step profiling analysis. The dependence of growth rate on substrate temperature is shown in figure 6. As shown from the results, though TiO$_2$ thin films required the highest activation energy (~78 kJ mol$^{-1}$) [16] for film formation of any other thin film, it was possible to make TiO$_2$ thin films on the substrate rapidly. In the case of HfO$_2$ thin film, the film deposition occurred at low temperature and the lowest activation energy (~45 kJ mol$^{-1}$) [15]. However, it has slower film growth rate than that of TiO$_2$ deposition. In the case of ZrO$_2$, in spite of the film formation energy being calculated as ~54 kJ mol$^{-1}$,
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Figure 5. SEM images of TiO$_2$, ZrO$_2$ and HfO$_2$ thin films grown by Ti(0’Pr)$_4$, Zr(0’Pr)$_2$(tbaoac)$_2$ and Hf(O’Bu)$_4$ on Si(100) substrates, respectively. (a) TiO$_2$ thin film grown at 350 °C for 4 h, (b) TiO$_2$ thin film grown at 450 °C for 4 h, (c) ZrO$_2$ thin film grown at 450 °C for 2 h, (d) ZrO$_2$ thin film grown at 500 °C for 2 h, (e) HfO$_2$ thin film grown at 200 °C for 1 h, and (f) HfO$_2$ thin film grown at 350 °C for 1 h.

Figure 6. The Arrhenius plots of TiO$_2$, ZrO$_2$ and HfO$_2$ thin films grown by Ti(0’Pr)$_4$, Zr(0’Pr)$_2$(tbaoac)$_2$ and Hf(O’Bu)$_4$ on Si(100) substrates, respectively.

it required high deposition temperature for film formation and it showed very slow growth rate.

In this study, we have studied the selectivity tendency of various metal oxide thin films on Si(100) surfaces which were patterned by OTS as a passivation layer. We expected that the difference in chemical properties of a patterned SAMs and bare Si(100) surfaces suggest difference nucleation and growth behaviour when the substrates were deposited in a MOCVD reactor. And the taken metal-organic precursors are stronger Lewis acids than silicon surfaces on account of their lower electronegativity. Therefore nucleophilic attack at the metal is facilitated from the Si–OH surfaces [17]. It means that a chemical reaction between the precursors and silicon surface occurs more easily than with the –CH$_3$ terminal groups of OTS SAMs surface. Moreover, β-hydrogen in the precursors can react with the –OH base element of Si(100) surface, and help the precursors make metal oxide thin films on bare Si(100) surfaces. In this experiment, the selectivity tendency was observed to be in the order of TiO$_2 >$ HfO$_2 >$ ZrO$_2$. It can be understood as follows. The molecular weight (M.W.) of Ti(0’Pr)$_4$ is smaller than those of other precursors and Ti coordinates the four ligands with small volume. It means that the –OH group on Si(100) surface can react easily with Ti due to less steric hindrance. Therefore, they can enhance the growth rate of TiO$_2$ thin film on the Si(100) surface. And because Ti(0’Pr)$_4$ has small M.W., it induced very small amount of London force and good mobility on the OTS SAMs surface, that is, this precursor is very difficult to react with OTS SAMs surface. These factors activated the TiO$_2$ film growth rate on the Si(100) surface and brought good selectivity of TiO$_2$. On the other hand, Zr(0’Pr)$_2$(tbaoac)$_2$ for ZrO$_2$ thin film is a very heavy molecule and has a coordinate number six. Heavy M.W. could induce high London force and low molecular mobility on the OTS SAMs surface. Moreover, –OH of Si(100) surface cannot attack easily at Zr owing to its steric hindrance. These factors required long nucleation time for ZrO$_2$ thin film formation on Si(100) surface, but on
the other hand they give OTS SAMs the high probability of ZrO$_2$ thin film deposition. It means less selectivity tendency than those of TiO$_2$ and HfO$_2$. Hf(O'Bu)$_4$ is heavier and has bigger ligands than those of Ti(O'Pr)$_4$. Because the M.W. of Hf itself is bigger than those of Ti and Zr, Hf has stronger acid character than Ti and Zr. It brings good reactivity with –OH elements, but the growth rate of HfO$_2$ thin film was lower than the growth rate of TiO$_2$ thin film. That is, this precursor needed relatively long nucleation time on the Si(100) surface than TiO$_2$ deposition. If it is deposited for a long time (over 2 h), Hf(O'Bu)$_4$ can react with not only the OTS SAMs area but also the Si(100) surface.

4. Conclusions

Selective growths of various metal oxides such as TiO$_2$, ZrO$_2$ and HfO$_2$ thin films were carried out on a patterned Si(100) surface by a combination of MOCVD and µCP method. The selectivity of deposited thin films from various metal-organic precursors was mainly studied from the data of temperature dependence of the growth rate. In this study, the selectivity tendency was observed to be in the order of TiO$_2$ > HfO$_2$ > ZrO$_2$. The observation was explained by means of growth rate of thin films and nature of the precursors. The main factors to influence the selectivity of oxide thin films were not only deposition temperature but also the growth rate of thin film, M.W. of precursors and steric hindrance of centre-metal of precursors. If all the factors such as low molecular weight, rapid growth rate and low steric hindrance of centre-metal of the precursor were present, good selective growth of metal oxide thin films on OTS patterned Si(100) substrates could be obtained.

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References