Selective MOCVD of titanium oxide and zirconium oxide thin films using single molecular precursors on Si(100) substrates

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Abstract

Titanium oxide (TiO\textsubscript{2}) and zirconium oxide (ZrO\textsubscript{2}) thin films have been deposited on modified Si(100) substrates selectively by metal-organic chemical vapor deposition (MOCVD) method using new single molecular precursor of [M(O\textsubscript{i}Pr)\textsubscript{2}(tboaoc)\textsubscript{2}] (M = Ti, Zr; tboaoc = tertiarybutyl-acetoacetate). For changing the characteristic of the Si(100) surface, micro-contact printing (µCP) method was adapted to make self-assembled monolayers (SAMs) using an octadecyltrichlorosilane (OTS) organic molecule which has –CH\textsubscript{3} terminal group. The single molecular precursors were prepared using metal (Ti, Zr) isopropoxide and tert-butylacetoacetate (tboaocH) by modifying standard synthetic procedures. Selective depositions of TiO\textsubscript{2} and ZrO\textsubscript{2} were achieved in a home-built horizontal MOCVD reactor in the temperature range of 300–500 °C and deposition pressure of 1–30–3 Torr. N\textsubscript{2} gas (5 sccm) was used as a carrier gas during film depositions. TiO\textsubscript{2} and ZrO\textsubscript{2} thin films were able to deposit on the hydrophilic area selectively. The difference in surface characteristics (hydrophobic/hydrophilic) between the OTS SAMs area and the SiO\textsubscript{2} or Si–OH layer on the Si(100) substrate led to the site-selectivity of oxide thin film growth.

Keywords: A. Oxides; A. Thin film; B. Vapor deposition; D. Surface properties

1. Introduction

Oxide materials have a wealth of 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 [1,2]. Titanium dioxide (TiO\textsubscript{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 band gap, high refractive index, and good insulating properties. Moreover, it is useful in fabricating dielectric capacitors in microelectronic devices because of its high dielectric constant. Up to now, TiO\textsubscript{2} has been extensively studied for its interesting electric, magnetic, catalytic, and electrochemical properties [3–6]. Based upon these properties, a variety of technological applications of TiO\textsubscript{2} thin film are possible. Also, zirconium oxide (ZrO\textsubscript{2}) has been extensively studied for use as a silicon dioxide replacement in the gate-oxide insulating layer in complementary metal oxide semiconductor (CMOS) devices. ZrO\textsubscript{2} has high dielectric constants and a high-energy band gap [7].

As these good properties and applications, metal oxide thin films have been deposited by several physical and chemical deposition techniques [8–11]. Among them, chemical vapor deposition (CVD) technique using metal-organic compound as a precursor (MOCVD) has many advantages, such as good conformal coverage, the possibility of epitaxial growth and selective deposition and the application to large-area deposition, etc. Also this method is low cost and is easy to control the deposition/growth parameters. Thus, the MOCVD method is well known as the one of the most powerful techniques and is suitable for
stoichiometric and micro-structured thin film deposition. The patterning of thin film is of considerable scientific and technological interest. Soft lithography is a method to make micro/nano size patterns and structures simply using organic materials without involving high energy. In particular, micro-contact printing (μCP) is a very convenient and nonphotolithographic technique that can generate patterned features of self-assembled monolayers (SAMs) on various surfaces [12]. The ability to control the wettability of a solid surface is important and useful in a range of technological applications [13–15]. In addition, the μCP technique shows that hydrophobic patterns with micron dimensions can be formed on hydrophilic surfaces avoiding the use of photolithographic-type procedures. Xia and Whitesides [13] and Folch and Schmidt [16] presented the current state of development of soft lithographic techniques and areas in which these techniques find applications. The authors suggested the μCP technique could apply to micro-electro-mechanical system (MEMS), sensors, and microelectronics with large patterning features over 100 μm scale, because small-area wafer and large linewidths are perfectly suited for most those applications.

Earlier, we reported deposition of patterned TiO2 thin films using titanium(IV) isopropoxide [Ti(O"Pr)4] by MOCVD on Si(100) substrates where the surface was first modified by an octadecyltrichlorosilane (OTS) [17]. The aim of the work presented here is to fabricate thin films and micro/nano patterning of TiO2 and ZrO2 thin films by using of new single molecular precursors. Herein, we report that site-selective MOCVD of TiO2 and ZrO2 thin films using bis-isopropoxy-bis-tertiarybutyl-acetoacetate titanium [Ti(O"Pr)2(tboaoc)2] as precursors on OTS patterned Si(100) substrates.

2. Experimental

The polydimethylsiloxane [-Si(CH3)2O-]n (PDMS) stamps were used for μCP and OTS [CH3(CH2)17SiCl3] SAMs were fabricated according to a previously reported procedure [13]. A solution of OTS in dry hexane was used as the “ink.” The OTS solution was applied to the PDMS stamp using a spin coater. Then, the stamp was brought into contact with the Si(100) substrate whose surface contains a native oxide layer. The thermal stability of the OTS SAMs on the Si(100) substrate is so strong that it can endure around 450 °C in a vacuum condition. After printing, thin films were deposited on these OTS patterned Si(100) substrates by MOCVD using new metal-organic precursors, [M(O"Pr)2(tboaoc)2] (M = Ti, Zr; tboaoc = tertiarybutyl-acetoacetate) as a single molecular precursor. Ti(O"Pr)2(tboaoc)2 exists as pale-yellow crystalline solids at room temperature, having a melting point 58 °C and Zr(O"Pr)2(tboaoc)2 is a white crystalline solid with 45 °C melting point. The details of the synthesis and characterization of the compounds is reported in the literature [18,19]. The OTS patterned Si(100) substrate was pre-treated with ethanol and de-ionized (DI) water in an ultrasonic cleaner without acid treatment to protect the OTS patterning from being destroyed. The CVD experiments were performed in a homebuilt MOCVD system. Nitrogen was used as the carrier gas (5 sccm). The base pressure of the MOCVD apparatus was 1 × 10−3 Torr, and the working pressure was kept in the range of 30–50 mTorr. The precursor bottle was heated at 80 °C. The deposition of TiO2 thin films was carried out at 300–400 °C for 0.5–1 h. And the depositions of ZrO2 thin films were performed at 450–500 °C for a period of 2–4 h. The as-grown films were characterized by optical microscopy (OM), scanning electron microscopy (SEM), energy dispersive X-ray (EDX), atomic force microscopy (AFM) and micro-Raman spectroscopy.

3. Results and discussion

Selectively deposited TiO2 thin films can be identified by optical microscopy (OM). Fig. 1 shows an OM image of the deposited TiO2 thin film that was selectively grown on the OTS patterned Si(100) substrate at 400 °C for 1 h. The relatively dark area corresponds to the TiO2 deposited area and the bright area is OTS SAMs area.

SEM and AFM analyses were performed to see the surface morphologies of the selectively deposited TiO2 thin films. Fig. 2 shows the SEM image and EDX data (see inset) of the selectively grown TiO2 thin film on the OTS patterned Si(100) substrate. It was observed that the images (which consist of two different contrasts shown in Fig. 2) match well with the OM data. Moreover, it is seen that boundary shape between the OTS SAMs area and the TiO2 deposited area is also very sharp and clear. In order to identify the composition of both dark (TiO2 film) and bright areas (OTS SAMs), we utilized the EDX analysis shown in the inset in Fig. 2. In the case of bright area, the atomic ratio (%) of Ti and O was nearly 1:2, while in the dark area there was no evidence of Ti and O elements.

![Fig. 1. Optical microscope image of a TiO2 thin film deposited on the OTS patterned Si(100) substrate. The dark image is TiO2 deposited area and the bright image is OTS SAMs area.](image-url)
This is a good agreement with reported data of selective growth of TiO$_2$ thin film with Ti(O$i$Pr)$_2$(tboa)$_2$ [18] and of the CVD grown TiO$_2$ thin films with Ti(O$i$Pr)$_4$ [20].

Fig. 3(a) shows the 3D AFM image of the selectively grown TiO$_2$ thin film on OTS SAMs patterned Si(100) substrate at 400 $^\circ$C. The selective deposition of thin film and the sharp boundary between TiO$_2$ thin film area and OTS SAMs area was clearly seen. Fig. 3(b) also shows the 2D AFM image obtained from the same film as Fig. 3(a).

From the images of Fig. 3(a) and (b), also we can see two different contrasts similar to SEM images, indicating good selectivity. With the height profile (see inset) of the 2D AFM image, we can reconfirm the selective growth of TiO$_2$ thin film and the TiO$_2$ thin film was able to selectively deposit on 10 $\mu$m area with thickness of about 120 nm.

The clear and convincing evidence of selective growth was obtained by micro-Raman analysis with a 514 nm laser and 20 mW power. Fig. 4 shows the micro-Raman spectra of the Si(100) substrate (a), OTS SAMs printed area (b) and TiO$_2$ deposited area (c), respectively. In the case of (a) and (b), there were no characteristic bands except for the peaks originated from the Si(100) substrate. However, in Fig. 4(c), we clearly found that the three bands corresponding to the anatase TiO$_2$ Raman active fundamental modes, are recorded at 144 cm$^{-1}$ ($E_g$), 399 cm$^{-1}$ ($B_{1g}$), and 639 cm$^{-1}$ ($E_g$). The band positions were in very a good agreement with published data on either polycrystalline powders or monocrystals [21,22]. Moreover, the bands due to rutile and brookite phase of TiO$_2$ were not observed. With these data, we were able to conclude that the anatase phase TiO$_2$ thin film was able to mainly grow on the Si(100) substrate on which OTS SAMs were not covered, strictly speaking, a native oxide layer on Si(100) surface. This result proved the selectivity of TiO$_2$ thin film on the OTS patterned Si(100) substrate.

Selectivity of deposited ZrO$_2$ film can be identified by optical microscopy (OM) images. Fig. 5 shows an OM image of the deposited ZrO$_2$ films on OTS patterned Si(100) substrate at 450 $^\circ$C for 2 h. It shows contrast between OTS SAMs area and ZrO$_2$ thin films deposited region. The relatively dark area corresponds to the ZrO$_2$ deposited area and the bright area is OTS SAMs area.

Fig. 6 shows the SEM images of selectivity grown on OTS patterned Si(100) substrate. In the case of (a), grown at 450 $^\circ$C for 2 h, it shows that boundary shape between the
OTS SAMs area and ZrO₂ deposited area is clear. However, as the deposition time was increased up to 4 h, the boundary became very unclear. It means the ZrO₂ was able to deposit both hydrophilic area and hydrophobic area. We can suggest that the terminal group of OTS was oxidized and changed its character from hydrophobic to hydrophilic or removed from the substrate surface because the high deposition temperature and long deposition time [25]. The morphology of ZrO₂ thin film grown on Si(100) substrate was denser and smoother than that of ZrO₂ thin film grown on OTS SAMs surface.

XPS survey spectrum analysis was carried out of the as-deposited ZrO₂ film grown on Si(100) substrate at 450 °C (not shown here). The strong Zr₃d and O₁s peaks were clearly indicated. However, C₁s peak clearly appeared around 300 eV binding energy, we can guess that the carbon comes from the precursor during depositions and/or surface contamination from the air. Also, the O₁s and Zr₃d high-resolution XPS spectra were performed (not shown here). In the case of O₁s, there are two oxidation states attributed to O²⁻ and OH⁻ species at the binding energy of about 532 and 530 eV. We can ensure that the OH⁻ peak is just a surface contamination peak probably originated from H₂O in the air. The Zr₃d₅/₂ peak observed as a single peak at binding energy of 182.2 eV, which is a good agreement to Zr⁴⁺.

Fig. 7 shows the 3D AFM image of selectively grown ZrO₂ thin film on OTS SAMs patterned Si(100) substrate at 450 °C for 2 h. The selectivity of thin film and the sharp boundary between ZrO₂ thin film area and OTS SAMs are clearly distinguished. The thickness of deposited ZrO₂ thin film was approximately 30–40 nm. The growth rate of ZrO₂ thin films using Zr(OPr)₂(tbaac)₂ was much slower than that of TiO₂ thin films.

OTS SAMs have been demonstrated as a promising candidate for a MOCVD resist layer which can block the surface functional groups that are necessary for nucleation.

Fig. 5. OM images of a ZrO₂ thin film deposited on the OTS patterned Si(100) substrate.

Fig. 6. SEM image of a ZrO₂ thin film deposited on the OTS patterned Si(100) substrate at (a) 450 °C for 2 h and (b) 450 °C for 4 h.

Fig. 7. 3D and 2D AFM images of selective growth of a ZrO₂ thin film on Si(100) substrate.
and growth during the deposition [23]. In this experiment, OTS can prevent nucleation for TiO$_2$ and ZrO$_2$ thin film on the SAMs surfaces because it has hydrophobic terminal group (–CH$_3$), i.e., there are no reaction factors for chemisorption between the metal-organic (MO) precursors and –CH$_3$ groups. But the MO precursors can obtain electrons from the “base” originated from native oxide layers on the Si(100) surface and they can make chemisorptions with substrate very strongly. After all, thin film is able to be formed on it. However, OTS SAMs are weak in respect of thermal stability over 450 °C [25], they should change their identities or make some defects on the OTS SAMs area. Therefore, it is difficult to make thin films selectively on substrates by combination of μCP and MOCVD methods at high temperatures. Thomas et al. showed that Ti(O\textit{Pr})$_2$(tbaoc)$_2$ precursor showed slightly superior properties in terms of evaporation behavior, deposition temperature, and smaller amount of residue material than those of Zr(O\textit{Pr})$_2$(tbaoc)$_2$ precursor [24]. And Zr(O\textit{Pr})$_2$(tbaoc)$_2$ precursor could induce high van der Waals force with OTS SAMs surface and low molecular mobility on the OTS SAMs area owing to its high molecular weight compared to Ti(O\textit{Pr})$_2$(tbaoc)$_2$. These disadvantage factors should require a long nucleation time on the Si(100) substrate and cause less site-selective deposition than that of TiO$_2$ in our experiment.

4. Conclusions

We successfully deposited patterned TiO$_2$ and ZrO$_2$ thin films directly using a combination method of μCP and MOCVD methods. New developed precursors of [M(O\textit{Pr})$_2$(tbaoc)$_2$, M = Ti, Zr] were used as precursors for TiO$_2$ and ZrO$_2$ thin films. In the case of TiO$_2$ deposition, it showed a good selectivity growth on the patterned Si(100) substrate. The boundaries between the OTS SAMs area and TiO$_2$ deposited area were very clean cut and sharp without any breaks. The micro-Raman spectroscopy and the EDX data showed that the deposited TiO$_2$ thin films were stoichiometric with anatase phase. In the case of ZrO$_2$ thin films, they showed a selective deposition on the substrate as deposition time below 2h; however, the selectivity disappeared above 2h. It means that OTS should change or lose its identity due to high temperature and/or long deposition time. Even though the combination of MOCVD and μCP is a very convenient technique to make micro-size structures without involving photolithographic-type procedures, there are some limitations such as deposition temperature and deposition time. However, it is expected that the combination of μCP of SAMs and MOCVD is a better method for fabricating micro-size, various functional thin films at low temperatures.

Acknowledgments

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References