Atomic Layer Deposition of TiO$_2$ Thin Films from Ti(O^{i}Pr)$_2$(dmae)$_2$ and H$_2$O

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TiO$_2$ thin films were grown on Si (100) substrates by atomic layer deposition using [Ti(OPr^i)$_2$(dmae)$_2$] and water as precursors. The thickness, chemical composition, crystalline structure, and morphology of the deposited films were investigated by transmission electron microscopy, UV spectrometry, X-ray photoelectron spectroscopy, X-ray diffraction, and atomic force microscopy. The results show that TiO$_2$ ALD using [Ti(OPr^i)$_2$(dmae)$_2$] as a precursor is self-controlled at temperatures of 100-300 °C. At the growth temperatures below 300 °C, the surface morphology of the TiO$_2$ films is smooth and uniform. The TiO$_2$ film was grown with a preferred orientation toward the [101] direction at 400 °C.

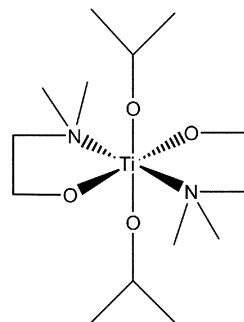**Key Words :** Atomic layer deposition, TiO$_2$, Precursor

Introduction

Thin films of titanium dioxide (TiO$_2$) have high refractive index, excellent transmittance in the visible and near-IR frequency, and high chemical stability.[1] They have been shown to be useful as anti-reflection coating, sensors, and photocatalysts.[2] The TiO$_2$ thin film is also a promising material for the development of microelectronics including as an alternative to silicon dioxide in the gate dielectric of metal oxide semiconductor field effect transistors (MOSFETS), due to its high dielectric constant.[3] Moreover, titanium oxide is a constituent of important multicomponent oxides such as BaTiO$_3$ and SrTiO$_3$, which are well known to be ferro-electrics.[4]

There have been several reports on atomic layer deposition (ALD) of TiO$_2$[5-9] although TiO$_2$ films were more frequently prepared by chemical vapor deposition.[10-12] The ALD is a gas-phase thin film deposition method by using self-controlled surface reactions. During the past decade the ALD has attracted considerable attention as a method manufacturing of high-quality thin films and producing tailored molecular structures.[13-16] The ALD method relied on sequential saturated surface reactions which result in the formation of a monolayer in each sequence. The successive self-controlled growth mechanism in the ALD inherently eliminates gas phase reactions. Elimination of gas phase reactions results in emphasizing the importance of surface reaction. As a consequence, the ALD process is very sensitive to precursors as well as surface conditions of the substrates. The ALD of TiO$_2$ thin films has been carried out using TiCl$_4$, [Ti(OEt)$_4$], and [Ti(OPr^i)$_4$], as titanium precursors. There are a number of major differences associated with the use of these precursors: the temperature range for the self-controlled growth, growth rate, film crystallinity, and surface morphology.

Jones *et al.*[17] reported on the preparation of TiO$_2$ thin films

Figure 1. The proposed structure of the precursor [Ti(OPr^i)$_2$-(dmae)$_2$].

using modified alkoxide of titanium, [Ti(OPr^i)$_2$(dmae)$_2$] (dmae = dimethylaminoethoxide), as titanium precursor in liquid injection MOCVD and found it to be a better source than other titanium CVD sources previously reported. In the present study, we have investigated the contribution of the precursor, [Ti(OPr^i)$_2$(dmae)$_2$], to the growth rate, film crystallinity, and surface morphology in the ALD of the TiO$_2$ thin films on Si substrates. The precursor, [Ti(OPr^i)$_2$(dmae)$_2$], exists as a monomeric complex with pseudo-octahedral coordination at the titanium and has an increased coordinative saturation at the titanium relative to Ti(OR)$_4$ compounds, as shown in Figure 1. Therefore, the precursor is more stable in air and moisture than conventional titanium precursors which need to prevent deterioration during storage and use. For comparison, the precursor, [Ti(OPr^i)$_4$], was also used in the ALD of the TiO$_2$ thin films on Si substrates.

Experimental Section

Precursor synthesis. The precursor, [Ti(OPr^i)$_2$(dmae)$_2$], was prepared by the procedures reported previously.[17] All manipulations were carried out under an inert atmosphere condition using a glove box or standard Schlenk techniques.

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Titanium isopropoxide [Ti(OPr^i)$_4$] and dimethylaminoethanol [HOCH$_2$CH$_2$N(CH$_3$)$_2$] (Hdmae) were used as received from Aldrich Chemicals, Inc. The solvents were distilled from sodium/benzophenone and degassed prior to use. The ^{1}H NMR spectra were recorded on a Bruker DPX 300 MHz spectrometer with chemical shifts referenced internally to benzene-d_6.

Hdmae was slowly added to a solution of titanium isopropoxide in n-hexane. The solution mixture was refluxed for 1 h and was then allowed to cool. Removal of all volatiles *in vacuo* resulted in a colorless liquid. The crude [Ti(OPr^i)$_2$-(dmae)$_2$] product was then purified by vacuum distillation. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 ^{o}C): δ 1.30 [12H, d, OCH(CH_3)$_2$], 2.23 [12H, s, OCH$_2$CH$_2$N(CH_3)$_2$], 2.54 [4H, t, OCH$_2$CH_2N-(CH$_3$)$_2$], 4.43 [4H, t, OCH_2CH$_2$N(CH$_3$)$_2$], 4.84 [2H, hept, OCH(CH$_3$)$_2$].

Atomic layer deposition of TiO$_2$ thin films. The Si substrates used for the film growth in this research were cut from n-type (100) wafers with resistivity in the range 1-5 Ωcm. The Si substrates were initially treated by a chemical cleaning process, which involves degreasing, HNO$_3$ boiling, NH$_4$OH boiling (alkali treatment), HCl boiling (acid treatment), rinsing in deionized water and blow-drying with nitrogen, proposed by Ishizaka and Shiraki[18] to remove contaminants and grow a thin protective oxide layer on the surface. The Si substrates were introduced into the atomic layer deposition (ALD) system (Genitech Cyclic 4000). The TiO$_2$ thin films were deposited onto the Si substrates using [Ti(OPr^i)$_2$(dmae)$_2$] and water as ALD precursors. Ar served both as a carrier and a purging gas. The [Ti(OPr^i)$_2$(dmae)$_2$] and water were evaporated at 80 and 20 ^{o}C, respectively. In order to find the pulse durations which were sufficient for the self-controlled film growth, the pulse times of the precursors were varied between 1 s and 10 s at 100 ^{o}C. In this study, the standard cycle consisted of 2 s exposure to [Ti(OPr^i)$_2$(dmae)$_2$], 5 s Ar purge, 2 s exposure to water, and 5 s Ar purge. The total flow rate of the Ar was 20 sccm. The TiO$_2$ thin films were grown at temperatures of 80-400 ^{o}C under 2 torr.

Characterization of TiO$_2$ thin films. Several analysis and characterization techniques were employed to investigate the TiO$_2$ thin films. The thickness of the TiO$_2$ films was measured by transmission electron microscopy (TEM, JEOL) and UV spectrometer (Scinco S-3100). X-ray photoelectron spectroscopy (XPS, VG ESCALAB MK II)[19] was applied to study the compositions and chemical states in the TiO$_2$ films. The surface morphology was investigated by atomic force microscopy (AFM, PSI CPII). X-ray diffraction (XRD, Rigaku RU-200BH) was carried out to determine the crystallinity of the TiO$_2$ films.

Results and Discussion

Self decomposition of [Ti(OPr^i)$_2$(dmae)$_2$]. The self control of the ALD becomes destroyed by the self decomposition of the precursor. The temperature where the thermal decomposition of the precursor becomes dominant was examined by
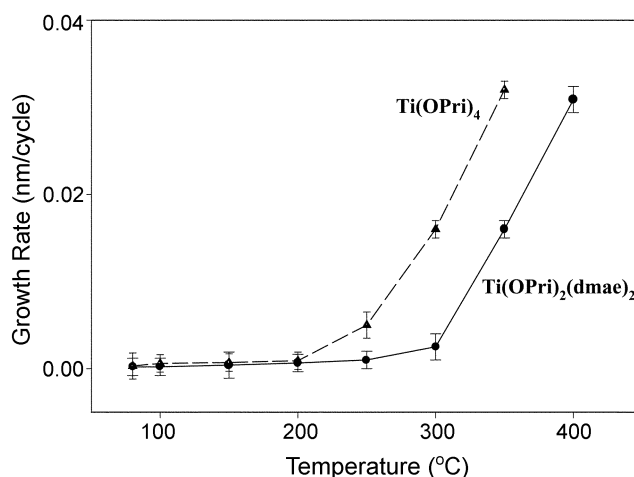

Figure 2. Temperature dependence of the growth rate for the TiO$_2$ films grown without water exposure. The cycle consisted of 2s exposure to [Ti(OPr^i)$_2$(dmae)$_2$], 5 s Ar purge, 2s exposure to Ar, and 5 s Ar purge.

measuring of the film growth rate without water exposure. The TiO$_2$ films were deposited onto the Si substrates using only [Ti(OPr^i)$_2$(dmae)$_2$] as the growth temperature increases. The cycle consisted of 2 s exposure to [Ti(OPr^i)$_2$(dmae)$_2$], 5 s Ar purge, 2 s exposure to Ar, and 5 s Ar purge. Figure 2 shows that the contribution of the self decomposition of the precursor, [Ti(OPr^i)$_2$(dmae)$_2$], is negligible below 300 ^{o}C. When the growth temperature is raised to 350 ^{o}C, the self decomposition of the precursor becomes dominant, which means that the transition temperature from ALD to CVD is around 350 ^{o}C. This observation suggests that the temperature range for TiO$_2$ ALD using [Ti(OPr^i)$_2$(dmae)$_2$] as a precursor is limited to below 350 ^{o}C. For comparison, the precursor, [Ti(OPr^i)$_4$], was also examined. The self-decomposition temperature of [Ti(OPr^i)$_4$] is about 50 ^{o}C lower than that of [Ti(OPr^i)$_2$(dmae)$_2$]. Therefore, the temperature range for TiO$_2$ ALD using [Ti(OPr^i)$_4$] as a precursor is limited to below 250 ^{o}C.
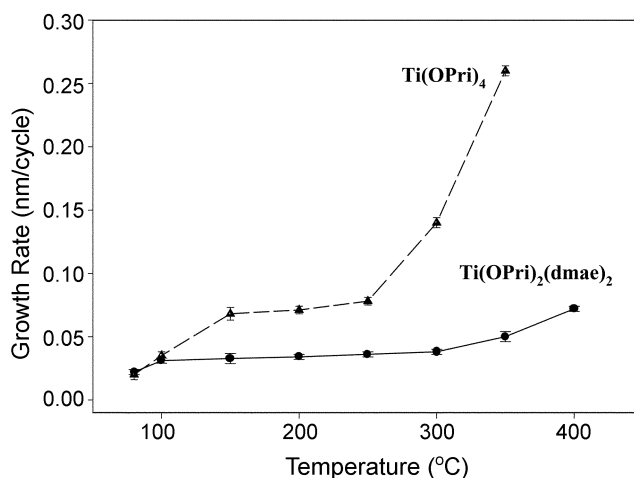

Figure 3. Temperature dependence of the growth rate for the TiO$_2$ films. The cycle consisted of 2s exposure to [Ti(OPr^i)$_2$(dmae)$_2$], 5 s Ar purge, 2s exposure to water, and 5 s Ar purge.
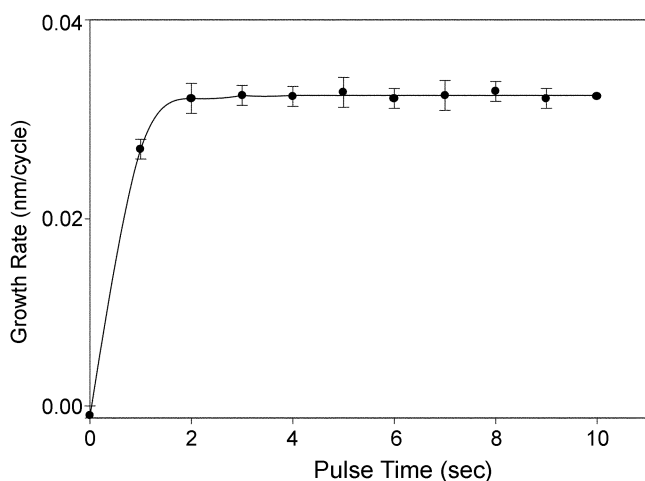
Figure 4. The growth rate as a function of the pulse duration for the TiO₂ films grown at 100 °C.

Growth rate of TiO₂ films. The TiO₂ films using $[Ti(OPr^j)_2(dmae)_2]$ and water were grown on Si (100) substrate at temperatures of 80-400 °C. The growth rate of the TiO₂ films was measured by TEM as the growth temperature increases. Figure 3 shows that a temperature-independent growth rate of 0.03 nm/cycle is obtained between 100 and 300 °C. To verify that the growth mechanism is really self-controlled, the pulse time of the precursor was varied between 1 s and 10 s at 100 °C. The film thickness per cycle is saturated when the pulse time exceeds 2 s, which indicates that the growth is self-controlled (Figure 4). These results suggest that TiO₂ ALD using $[Ti(OPr^i)_2(dmae)_2]$ as a precursor is self-controlled at temperatures of 100-300 °C. For comparison, the TiO₂ films using $[Ti(OPr^j)_4]$ and water were also grown on Si (100) substrate. The temperature-independent growth rate of 0.06 nm/cycle is obtained between 150 and 250 °C, as shown in Figure 3.

Surface composition of TiO₂ films. XPS analysis was performed to determine the composition of the TiO₂ films using $[Ti(OPr^i)_2(dmae)_2]$ as a function of growth temperature.
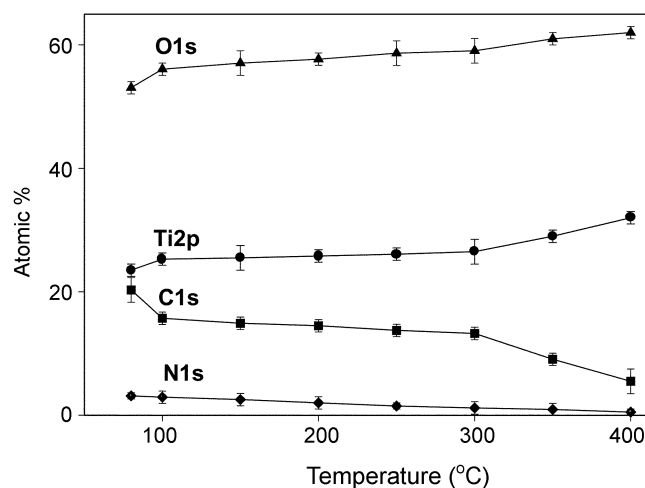
Figure 5 shows that the intensities of Ti(2p) and O(1s) peaks remain almost constant at about 100 to 300 °C and then increase above 350 °C. This XPS analysis is consistent with the behavior of the growth rate in that the growth rate of the TiO₂ ALD is independent of the growth temperature between 100 and 300 °C. The TiO₂ films contained relatively large amounts of carbon, and the intensity of the C(1s) peak slightly decreases at temperatures of 100-300 °C. When the growth temperature is raised to 350 °C, the intensity of C(1s) peak rapidly decreases and the N(1s) peak has almost completely disappeared. High resolution spectra of the O(1s) peak for the TiO₂ films are shown in Figure 6 as a function of growth temperature. The O(1s) region shows two peaks at 529.6 and 531.8 eV, which are assigned to titanium oxide and alkoxide species,[20,21] respectively. The O(1s) peaks remain almost intact in intensities and shapes between 100 and 300 °C. Above 350 °C, the O(1s) peak at 531.8 eV have decreased in intensity and almost disappeared at about 400 °C. These results indicate that the hydrolysis reaction of the ligands in the precursor, $[Ti(OPr^i)_2(dmae)_2]$, with water is not complete at temperatures below 350 °C.

Surface morphology of TiO₂ films. Evolution of the surface morphology of the TiO₂ films using $[Ti(OPr^i)_2(dmae)_2]$ was examined by atomic force microscopy (AFM) as the growth temperature increases (Figure 7). At the growth temperatures below 300 °C, the surface morphology of the TiO₂ films is smooth and uniform, and the root mean square (RMS) roughness of the surface is as low as 0.7 nm. When the growth temperature is raised to 350 °C, many small grains are observed and the surface morphology of the TiO₂ film becomes rough. For comparison, AFM analysis was also performed to examine the surface morphology of the TiO₂ films using $[Ti(OPr^i)_4]$ and water. At the temperatures above 250 °C, the TiO₂ films have a number of protrusions

Figure 5. The atomic concentrations as a function of growth temperature for the TiO₂ films.
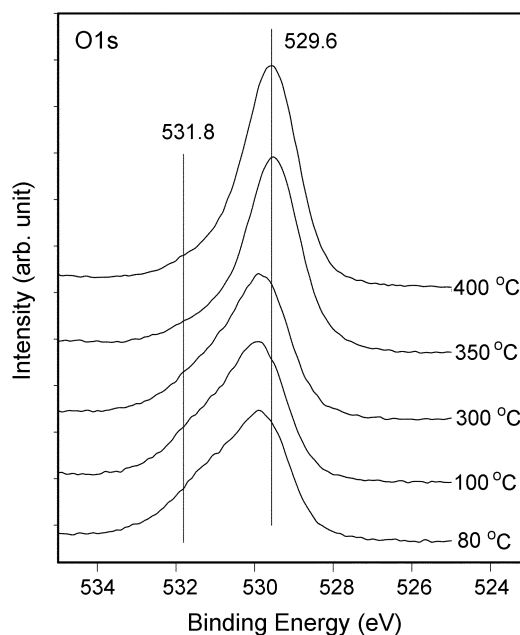
Figure 6. XP high-resolution spectra of the O(1s) region as a function of growth temperature for the TiO₂ films.

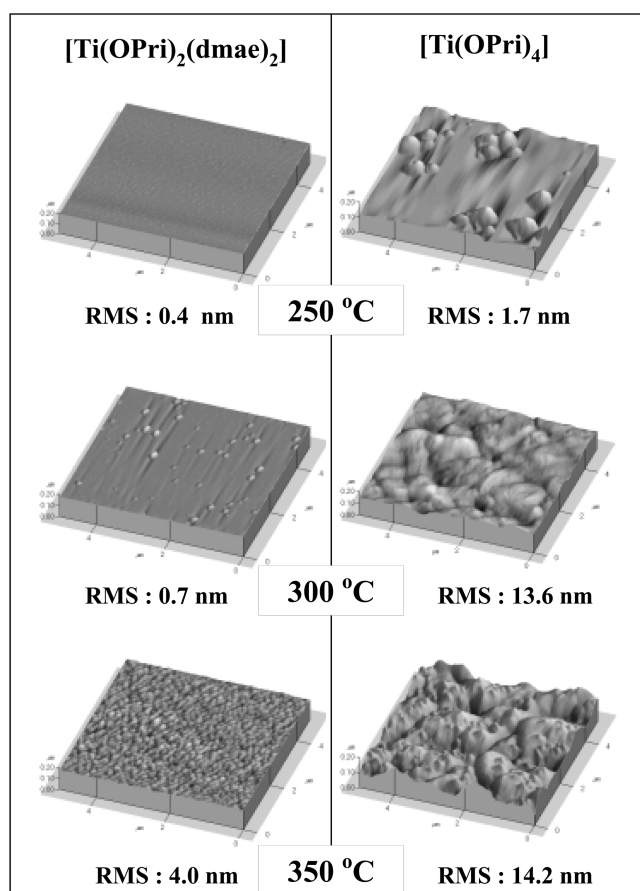**Figure 7**. AFM images of TiO₂ films grown at 250-350 °C.

Figure 8. XRD patterns of TiO₂ films grown at 200-400 °C.

and the RMS roughness of the surface increases as the growth temperature increases.

Crystal structure of TiO₂ films. XRD patterns for the TiO₂ films using [Ti(OPr^i)₂(dmae)₂] on Si (100) as a function of deposition temperature are shown in Figure 8. The films deposited at temperatures below 350 °C show no XRD peaks, indicating amorphous TiO₂ films were obtained at these temperatures. The XRD pattern of the film at 400 °C clearly displays one dominant peak at $2\theta = 25.4°$ corresponding to the anatase TiO₂(101) peak. It suggests that the crystalline anatase TiO₂ film was grown with a preferred orientation toward the [101] direction at 400 °C. XRD analysis was also performed to determine the crystalline structures for the TiO₂ films using [Ti(OPr^i)₄] and water. The XRD pattern of the film deposited at 250 °C or lower shows either weak peaks or no peaks at all, indicating that amorphous TiO₂ films were obtained at these temperatures. The XRD patterns of the films at 300 to 350 °C clearly display characteristic peaks of TiO₂ at $2\theta = 25.4°$, 38.8°, 48.0°, and 55.0° that are attributed to anatase TiO₂ (101), (112), (200), and (211), respectively. It suggests that polycrystalline anatase TiO₂ films were obtained at these temperatures.

Conclusion

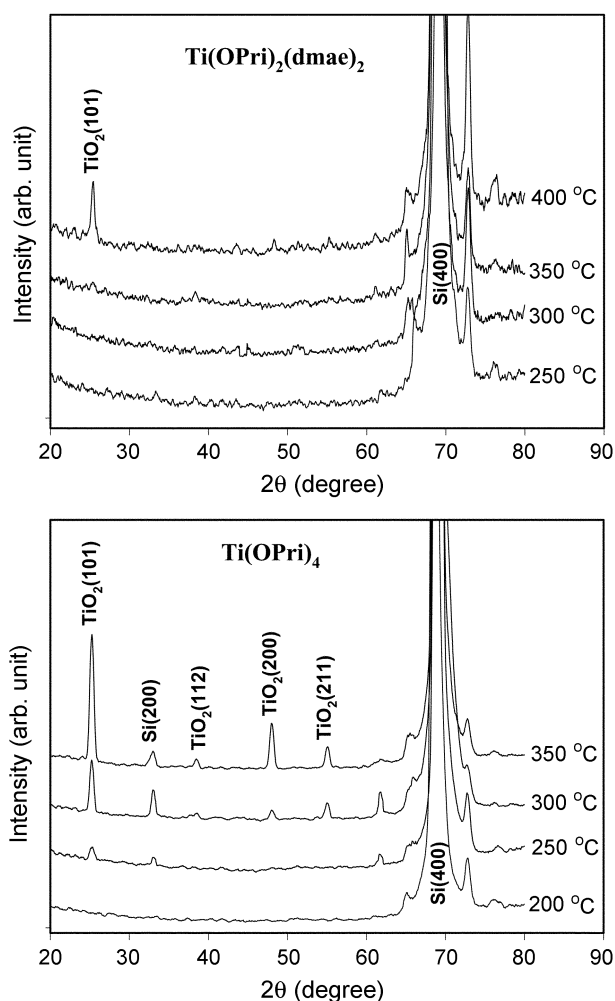The precursor [Ti(OPr^i)₂(dmae)₂], as a monomeric complex

with pseudo-octahedral coordination at the titanium, has been synthesized and employed to grow TiO₂ films on Si(100) by ALD. The self-decomposition temperature of [Ti(OPr^i)₂(dmae)₂] is about 350 °C, whereas that of [Ti(OPr^i)₄] is about 300 °C. The TiO₂ ALD using [Ti(OPr^i)₂(dmae)₂] as a precursor is self-controlled at temperatures of 100-300 °C. XPS analysis shows that the hydrolysis reaction of the ligands in the precursor, [Ti(OPr^i)₂(dmae)₂], with water is not complete at temperatures below 350 °C. AFM analysis shows that the surface morphology of the TiO₂ films using [Ti(OPr^i)₂(dmae)₂] is smooth and uniform at the growth temperatures below 300 °C. The XRD patterns of the TiO₂ films show that the film grown at 400 °C is predominantly orientated toward the [101] direction.

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