Atomic Layer Epitaxy Growth of Titanium Dioxide Thin Films from Titanium Ethoxide

Mikko Ritala* and Markku Leskelä

Department of Chemistry, University of Helsinki, P.O. Box 6, FIN-00014 Helsinki, Finland

Eero Rauhala

Accelerator Laboratory, University of Helsinki, P.O. Box 43, FIN-00014 Helsinki, Finland

Received January 3, 1994®

Atomic layer epitaxy (ALE) growth of titanium dioxide thin films was attempted using titanium ethoxide and water as precursors. Due to a slight self-decomposition of the titanium precursor, no completely self-controlled growth was achieved. However, the slowness of the self-decomposition process provided that the advantageous features of the ALE technique, *viz.*, accurate thickness control, reproducibility, film uniformity, and high film density, were not essentially deteriorated. The present process is compared with those exploiting $TiCl_4$ and titanium isopropoxide as titanium precursors.

Introduction

During the past decade atomic layer epitaxy (ALE) has attracted considerable attention as a method providing controlled growth of high-quality thin films onto large area substrates.[1-3] The characteristic feature of ALE is an alternate dosing of reactants onto the substrate. Between the reactant pulses the reactor is either purged with an inert gas or evacuated and when the experimental conditions are properly adjusted, only a chemisorbed monolayer of one reactant is retained on the substrate to react with the other reactant dosed subsequently. When the reaction cycle is repeated a solid film is deposited layer-by-layer. However, formation of a complete monolayer during one cycle is often prevented by the bulkiness of precursor molecules, and as a consequence, the growth rate is less than one monolayer per cycle.[1] Nevertheless, the film thickness is still controlled simply by the number of reaction cycles repeated, *i.e.*, the film growth is self-controlled. In addition to the convenient thickness control, the self-controlled nature of the film growth provides also that even complex-shaped, large-area substrates will be uniformly coated. It should be emphasized that even though the word epitaxy usually refers to the growth of single crystalline materials, the term ALE is used as a name of the deposition method covering all kind of films, *i.e.*, in addition to the real epitaxial also polycrystalline and amorphous films, deposited in a self-controlled manner using the alternate dosing of the reactants. In fact, the crystallinity of the film is strongly dependent on the substrate structure.[4,5]

Recently, we have studied ALE deposition of TiO_2 films using $TiCl_4$[4,6] and titanium isopropoxide ($Ti(OCH(CH_3)_2)_4$)[7] in combination with water as precursors. Both processes resulted in films with high densities as judged by means of high refractive indices, low hydrogen contents in the bulk of the films, and the close agreement of film thicknesses obtained from RBS and optical measurements. Also surface roughening arising from agglomerates developed during the early stages of the film growth was common for these processes. Nevertheless, some major differences were observed as well: (i) The thermal decomposition of $Ti(OCH(CH_3)_2)_4$ limited the temperature range for the self-controlled growth below 350 °C, while $TiCl_4$ was applicable within the whole temperature range studied extending up to 600 °C. (ii) The films deposited onto glass substrates from $Ti(OCH(CH_3)_2)_4$ were partially crystalline anatase already at 250 °C in contrast to the amorphous films obtained from $TiCl_4$ even at 600 °C. This difference was related to the bridging property of the alkoxide ligand which was assumed to facilitate ordering on the surface of the growing film. (iii) The growth rate obtained with $TiCl_4$ (0.56 Å/cycle) was higher than that obtained with $Ti(OCH(CH_3)_2)_4$ (0.30 Å/cycle) which was correlated to the smaller molecular size of $TiCl_4$.

The aim of the present work where titanium ethoxide ($Ti(OCH_2CH_3)_4$) was used as a precursor in ALE growth of TiO_2 was to study further the contribution of the titanium precursor to the growth rate and film crystallinity. Due to reduced steric hindrances ethoxide groups are more effective in acting as bridging ligands between metal cations than isopropoxide groups. As a result, $Ti(OCH_2CH_3)_4$ molecules are more strongly oligomerized than $Ti(OCH(CH_3)_2)_4$ molecules.[8] Apparently the same order of bridging property prevails also on the surface of the growing film, and therefore it seems possible that the films to be deposited from $Ti(OCH_2CH_3)_4$ might possess even more crystalline structure than those obtained from $Ti(OCH(CH_3)_2)_4$. On the other hand, the deposition rate to be achieved with $Ti(OCH_2CH_3)_4$ is expected, on basis of molecular sizes, to lie between those obtained with $TiCl_4$ and $Ti(OCH(CH_3)_2)_4$.

® Abstract published in *Advance ACS Abstracts*, March 15, 1994.

[1] Leskelä, M.; Niinistö, L. In *Atomic Layer Epitaxy*; Suntola, T., Simpson, M., Eds.; Blackie and Son Ltd.: Glasgow, 1990; p 1.

[2] Suntola, T. *Mater. Sci. Rep.* **1989**, *4*, 261.

[3] Suntola, T. *Thin Solid Films* **1992**, *216*, 84.

[4] Ritala, M.; Leskelä, M.; Nykänen, E.; Soininen, P.; Niinistö, L. *Thin Solid Films* **1993**, *225*, 288.

[5] Goodman, C. H. L.; Pessa, M. V. *J. Appl. Phys.* **1986**, *60*, R65.

[6] Ritala, M.; Leskelä, M.; Johansson, L.-S.; Niinistö, L. *Thin Solid Films* **1993**, *228*, 32.

[7] Ritala, M.; Leskelä, M.; Niinistö, L.; Haussalo, P. *Chem. Mater.* **1993**, *5*, 1174.

[8] Bradley, D. C.; Mehrotra, R. C.; Gaur, P. D. *Metal Alkoxides*; Academic Press: London, 1978.

0897-4756/94/2806-0556$04.50/0

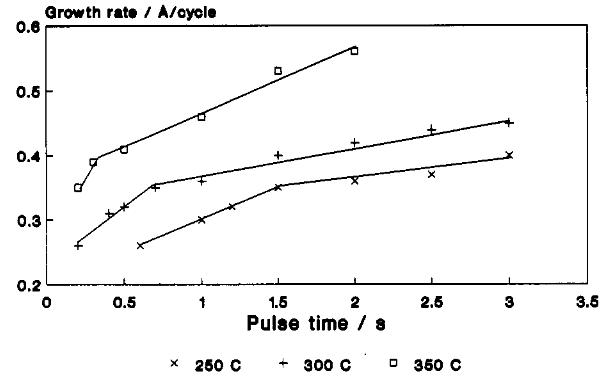

Figure 1. Growth rates as a function of pulse lengths at 250, 300, and 350 °C.

Experimental Section

TiO_2 films were deposited onto 5 × 5 cm^2 soda lime glass substrates using a commercial flow type reactor F-120 (Microchemistry Ltd., Espoo, Finland)[3] operated under a pressure of 10 mbar. Nitrogen served both as a carrier and a purging gas. $Ti(OCH_2CH_3)_4$ (STREM Chemicals) was evaporated from an open boat held at 83 °C inside of the reactor. The pulsing of the $Ti(OCH_2CH_3)_4$ vapor was accomplished by means of inert-gas valving.[3] Water vapor, generated in an external reservoir held at 20 °C, was dosed into the reactor through needle and solenoid valves. The reactant vapors were transported into the reaction zone through separate lines which crossed only about 1 cm ahead of the substrates.[3] Pulse and purge times were varied from 0.2 to 3.0 s and from 0.5 to 1.0 s, respectively.

A fitting method developed and described by Ylilammi and Ranta-aho[9] was exploited for evaluating film thicknesses and refractive indices from transmittance spectra which were measured within a wavelength region of 380–1100 nm with a Hitachi U-2000 spectrometer. Comparative thickness measurements were obtained by Rutherford backscattering spectrometry (RBS) of 2.0-MeV $^4He^+$ ions from the 2.5-MV Van de Graaff accelerator of the Accelerator Laboratory.[10] RBS was also used to verify the film stoichiometry. Carbon residues were analyzed by means of X-ray photoelectron spectroscopy (XPS) and argon ion sputtering using a PHI Small Spot ESCA 5400 electron spectrometer and a PHI 04-300 ion gun. XPS spectra were excited by nonmonochromatized Mg Kα radiation and measured using 89-eV analyzer energy and 0.5 eV channel width. The films were profiled for hydrogen by nuclear reaction analysis (NRA) technique using a $^{15}N^{2+}$ beam from the 5-MV tandem accelerator EGP-10-II of the Accelerator Laboratory to excite the 6.385-MeV resonance of the $^1H(^{15}N,\alpha\gamma)^{12}C$ reaction.[11] Crystal structure determination was carried out with a Philips MPD 1880 powder X-ray diffractometer using Cu Kα radiation. Film morphology was characterized with a NanoScope III atomic force microscope (AFM).

Results and Discussion

Film Growth. Figure 1 depicts growth rates per cycle as a function of the reactant pulse durations. At each three deposition temperatures studied, two linear regions were observed. Initially a rapid increase takes place until after a certain turning point the rise becomes slower. However, in contradiction with the ideal ALE mechanism the growth rate does not show saturation with increasing pulse times. It is quite obvious that the first region has its origin mainly in the exchange reactions between the sequentially dosed $Ti(OCH_2CH_3)_4$ and water, while the second region is attributed to the self-decomposition of $Ti(OCH_2CH_3)_4$. Naturally, only the former mechanism is desirable from the ALE process point of view since the self-decomposition is detrimental for the self-control of the film growth.

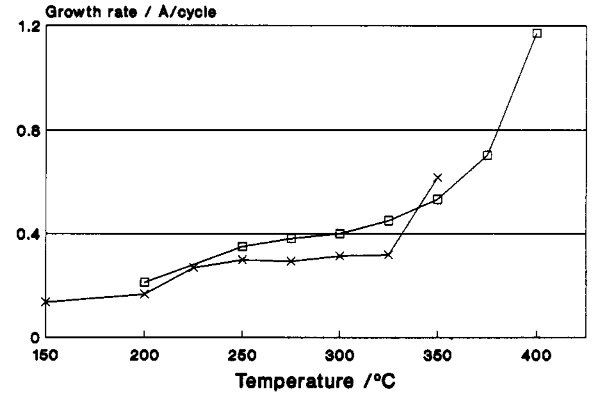

Figure 2. Temperature dependences of the growth rates for $Ti(OCH_2CH_3)_4$ (□) and $Ti(OCH(CH_3)_2)_4$ (×). The pulse times used, 1.5 and 0.6 s, respectively, were chosen in a way that at 250 °C the growth rates were located either in a decomposition dominated region ($Ti(OCH_2CH_3)_4$) or in a truly saturated region ($Ti(OCH(CH_3)_2)_4$).

The most decisive question in respect of the mechanism of the desired exchange reactions is whether the TiO_2 surface remains hydroxyl terminated or not after the water pulse. Unfortunately the compact design of our reactor[3] prevents the use of any *in situ* technique for answering this question. However, on the basis of the results reported in the literature,[12,13] it seems feasible that at temperatures used in the present study the surface remains partially hydroxyl terminated. Under these conditions the film growth is assumed to proceed via the following, schematically represented, irreversible exchange reactions:

$$n\ \text{-OH(s)} + Ti(OCH_2CH_3)_4(g) \rightarrow (\text{-O-})_nTi(OCH_2CH_3)_{4-n}(s) + nCH_3CH_2OH(g) \quad (1)$$

$$(\text{-O-})_nTi(OCH_2CH_3)_{4-n}(s) + (4-n)H_2O(g) \rightarrow (\text{-O-})_nTi(OH)_{4-n}(s) + (4-n)CH_3CH_2OH(g) \quad (2)$$

where –OH(s) represents surface hydroxyl and $n = 1$–3. It should be noted that once formed ethanol may also be dehydrated. On the other hand, if the film surface does become completely dehydroxylated after the water pulse, then the growth will apparently proceed via the chemisorption of $Ti(OCH_2CH_3)_4$ followed by its hydrolysis:

$$Ti(OCH_2CH_3)_4(g) \rightarrow Ti(OCH_2CH_3)_4(ads) \quad (3)$$

$$Ti(OCH_2CH_3)_4(ads) + 2H_2O(g) \rightarrow TiO_2(s) + CH_3CH_2OH(g) \quad (4)$$

where (ads) refers to chemisorbed species. Besides molecularly, $Ti(OCH_2CH_3)_4$ may chemisorb also dissociatively. Because the surface hydroxyl group density usually decreases smoothly with increasing temperature,[12,13] it seems also possible that the film growth involves both above-mentioned mechanisms in proportion to the density of hydroxyl groups, *i.e.*, with increasing temperature the contribution of the latter mechanism increases.

Figure 2 shows the temperature dependence of the growth rate when pulse times were fixed to 1.5 s, *i.e.*, to the value needed to surpass the turning point at 250 °C (*cf.* Figure 1). For comparison, the corresponding function

---

(9) Ylilammi, M.; Ranta-aho, T. *Thin Solid Films* **1993**, *232*, 56.

(10) Rauhala, E.; Keinonen, J.; Rakennus, K.; Pessa, M. *Appl. Phys. Lett.* **1987**, *51*, 973.

(11) Whitlow, H. J.; Keinonen, J.; Hautala, M.; Hautojärvi, A. *Nucl. Instrum. Methods Phys. Res., Sect. B* **1984**, *5*, 505.

(12) Parfitt, G. D. *Progr. Surf. Membr. Sci.* **1976**, *11*, 181.

(13) Morterra, C. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 1617.

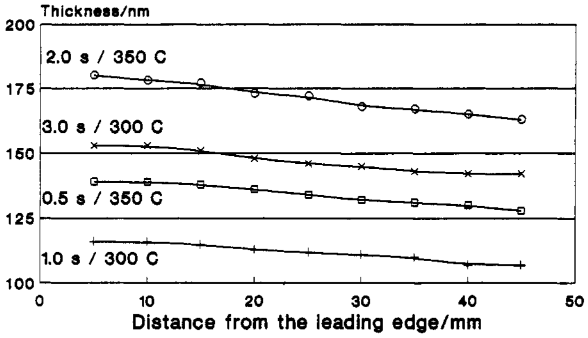

Figure 3. Thickness profiles of films grown by 3000 cycles at 300 and 350 °C with various pulse times.

for the process using $Ti(OCH(CH_3)_2)_4$ as a precursor is shown also.[7] Evidently, with the constant pulse times used no ALE window, *i.e.*, temperature region where the growth rate would be independent of the deposition temperature,[2] is found for $Ti(OCH_2CH_3)_4$, whereas with $Ti(OCH(CH_3)_2)_4$ the ALE window extends from 250 to 325 °C. Apparently, if temperatures below 250 °C were used, the contribution of $Ti(OCH_2CH_3)_4$ decomposition could be minimized but this would also decrease the rate of the exchange reactions, *i.e.*, the desired ALE process, to an unpractical low level.

Even though the film growth was not completely self-controlled, the resulting films had relatively good thickness uniformities even with pulse times considerably longer than those needed to reach the turning point (Figure 3). This is obviously due to the slowness of the decomposition process which provides that during the $Ti(OCH_2CH_3)_4$ pulse its partial pressure remains essentially constant over the whole substrate.

The elongation of the purge time from 0.5 to 1.0 s was not found to have any effect on the growth rate, indicating that while the chemisorbed monolayers were stable against desorption the physisorbed species were readily desorbed and purged out from the reactor. The effect of the $Ti(OCH_2CH_3)_4$ pressure was studied by varying the source temperature from 77 to 89 °C, but no changes could be observed even in the decomposition dominated region.

The thermal decomposition of $Ti(OCH_2CH_3)_4$ was studied further by dosing only $Ti(OCH_2CH_3)_4$ and nitrogen onto the substrate held at 300 °C. Repetition of 10 000 cycles consisting of 1.0-s $Ti(OCH_2CH_3)_4$ pulses and 0.2-s purging sequences resulted in a film with an atomic density of 120×10^{15} cm^{-2} (RBS) corresponding to a geometrical thickness of 14 nm for a film having the density of anatase. The decomposition rate obtained this way (0.014 Å/s) is smaller than the one (0.046 Å/s) which is evaluated from Figure 1, assuming that the observed growth in the latter of the two regions originates exclusively from the decomposition of $Ti(OCH_2CH_3)_4$. Even if this assumption is somewhat questionable, one can hardly correlate the difference observed completely to the way of decomposition rate determination. Instead, there is a possibility that the TiO_2 surface may have a catalytic effect on the decomposition process like it is known to have on decomposition of $Ti(OCH(CH_3)_2)_4$.[14,15] When the process is carried out in an ALE mode, *i.e.*, both $Ti(OCH_2CH_3)_4$ and water are alternately dosed into the reactor, the substrate becomes rapidly covered by the TiO_2 film, and therefore the catalyzed process is more pronounced than when $Ti(OCH_2CH_3)_4$ alone is pulsed onto the substrate. One should also consider the possible effect of water residues which inevitably exist in the reactor during the ALE process. However, on the basis of the comparison with the reaction rate between $Ti(OCH_2CH_3)_4$ and the intentionally dosed water, *i.e.*, with the growth rate observed in the exchange reaction dominated region, it seems very unlikely that the residual water pressure could be high enough to account for the difference observed.

An Arrhenius plot of the decomposition rates evaluated from Figure 1 as described above gave an apparent activation energy of 30 kJ mol^{-1} for the decomposition of $Ti(OCH_2CH_3)_4$. Despite some uncertainty arising from the fact that only three temperatures were studied, the activation energy evaluated is in good agreement with that, 28 kJ mol^{-1}, obtained by Hwang and Kim[16] for the reaction-controlled decomposition of $Ti(OCH_2CH_3)_4$. On the basis of a linear relationship found between TiO_2 deposition rate and the partial pressure of $Ti(OCH_2CH_3)_4$, Hwang and Kim postulated a decomposition mechanism where $Ti(OCH_2CH_3)_4$ is adsorbed in a molecular form and, subsequently, decomposed unimolecularly into TiO_2 and volatile byproducts.[16] However, with comparable $Ti(OCH_2CH_3)_4$ pressures, the decomposition rates were about 2 orders of magnitude higher than those found in the present study. This difference may be correlated to the total pressures of the reactors since Hwang and Kim carried out their study at atmospheric pressure whereas the pressure in our reactor was 2 orders of magnitude lower, *i.e.*, 10 mbar. Therefore, it seems feasible that the decomposition could proceed in a way proposed for the decomposition of $Ti(OCH(CH_3)_2)_4$,[17,18] *i.e.*, via activation by bimolecular gas-phase collisions followed by unimolecular adsorption and decomposition of the activated species. When the collisional gas-phase activation acts as a rate-limiting step, the decomposition rate is a function of the density of collisions the alkoxide undergoes. With increasing total pressure, collisions with carrier gas molecules become more frequent resulting in an increased decomposition rate.

On the basis of the above speculation, it should be possible to diminish the decomposition of $Ti(OCH_2CH_3)_4$ by reducing the total pressure of the reactor. A potential advantage of this approach, as compared with decreasing the deposition temperature, is that the desired exchange reactions might remain unaffected.

To carry out comparisons with the other titanium precursors, the contribution of the exchange reaction to the overall growth rate should be estimated. Slightly simplifying it can be assumed that the film growth can be divided into the two regions abruptly, *i.e.*, initially only the exchange reactions take place while after the turning point the film growth arises exclusively from the decomposition of $Ti(OCH_2CH_3)_4$. On the basis of this assumption, the growth rate corresponding to the turning point equals the value to which the growth rate would have been saturated in the ideal ALE process, *i.e.*, in absence of the decomposition. The estimations obtained at 250 and 300 °C (0.35 Å/cycle) are considered to be more reliable than the divergent value obtained at 350 °C (0.39 Å/cycle) where the pronounced decomposition process makes the above assumption more questionable.

---

(14) Komiyama, H.; Kanai, T.; Inoue, H. *Chem. Lett.* **1984**, 1283.

(15) Wadayama, T.; Mizuseki, H.; Hatta, A. *Vibr. Spectrosc.* **1991**, *2*, 239.

(16) Hwang, C. S.; Kim, H. J. *Ceram. Trans.* **1990**, *15* (*Mater. Processes Microelectron. Syst.*) 437.

(17) Siefering, K. L.; Griffin, G. L. *J. Electrochem. Soc.* **1990**, *137*, 814.

(18) Siefering, K. L.; Griffin, G. L. *J. Electrochem. Soc.* **1990**, *137*, 1206.

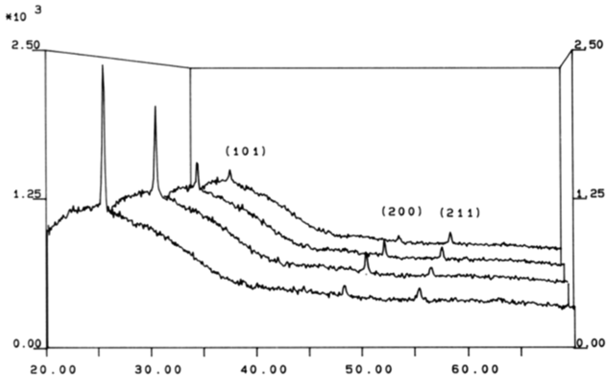

Figure 4. XRD patterns of films grown, from front to back, at 250, 300, 325, and 375 °C.

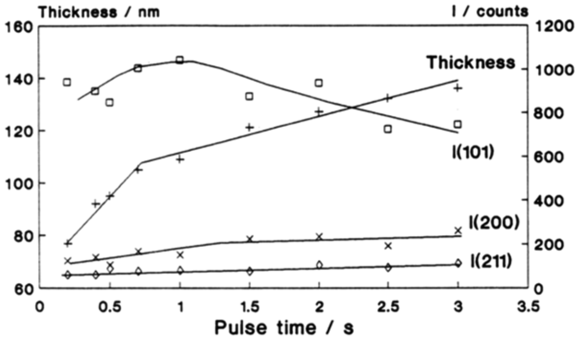

Figure 5. Film thicknesses and XRD peak intensities as a function of pulse times for films grown at 300 °C.

Film Structure and Properties. According to the XRD measurements films grown at or above 250 °C were partially crystalline anatase. The XRD patterns observed were similar to those obtained from films deposited using $Ti(OCH(CH_3)_2)_4$ as a precursor;[7] besides the most intense (101) reflection only relatively weak (200) and (211) reflections were detected (Figure 4). Since the intensities of even the strongest reflections from the films grown in the present study were only about one-third of those from films, with comparable thicknesses, deposited from $Ti(OCH(CH_3)_2)_4$ at 325 °C it is apparent that the films were not totally crystalline but consisted of anatase–amorphous mixtures.

The self-decomposition of $Ti(OCH_2CH_3)_4$ was found both to reduce the overall crystallinity of the films and to change their orientation as can be seen from Figure 4 where XRD patterns of films grown using 1.5-s pulses at various temperatures (*cf.* Figure 2) are shown. Because the film thicknesses lie within a narrow range of 120–140 nm one can neglect their contribution to the changes observed in XRD patterns which are, therefore, correlated to the deposition temperatures. An increase in the deposition temperature, *i.e.*, in the contribution of the decomposition process, causes a remarkable decrease in the intensity of the (101) reflection while the other two reflections remain essentially unchanged. The same effect can be seen also from Figure 5 which depicts the intensities of the three reflections as a function of the pulse times at 300 °C. To illustrate the location of the turning point, the film thicknesses are also shown. It is quite evident that increasing the pulse times in the decomposition-dominated region results in decreasing intensities of the (101) reflection while the minor peaks increase quite steadily within the whole pulse length range studied.

AFM studies revealed that notable surface roughening had occurred during the film growth. From Figure 6 it can be seen that the film grown using 1.0-s pulse times, *i.e.*, at exchange reaction dominated conditions, is rougher than that deposited using 3.0-s pulses, *i.e.*, at conditions where the contribution of $Ti(OCH_2CH_3)_4$ self-decomposition is significant (*cf.* Figure 1).

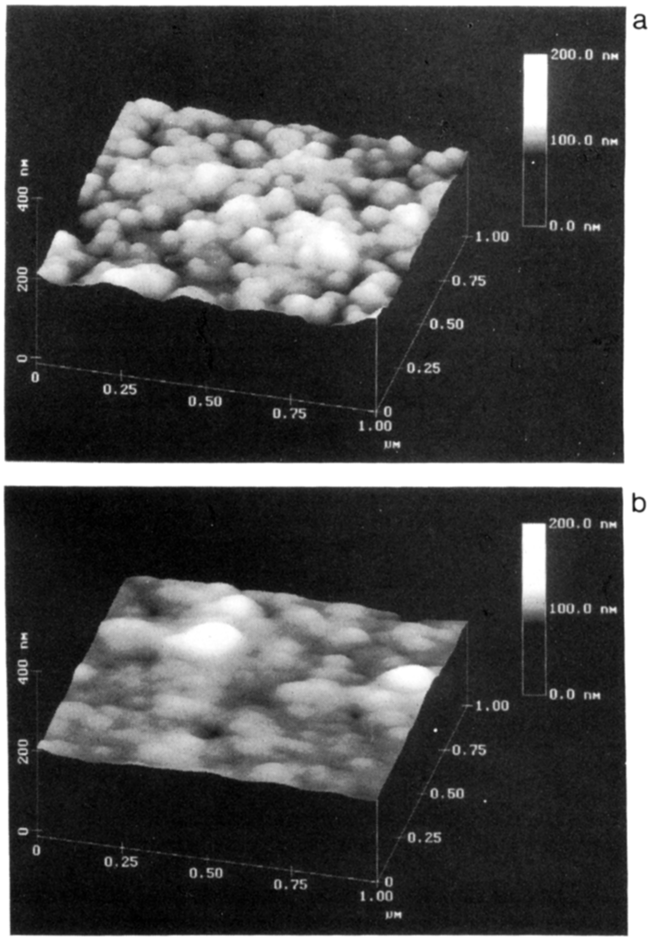

Figure 6. AFM images of films grown at 300 °C using 3000 deposition cycles with 1.0- (a) and 3.0-s (b) reactant pulses. The root-mean-square roughnesses are 9.3 and 7.0 nm, respectively.

The same kind of surface morphologies have been observed also for other ALE grown films, *viz*, for TiO_2 films prepared from other titanium precursors[6,7] and for ZrO_2 films grown from $ZrCl_4$ and water.[19] When the morphological development of TiO_2 films was studied in detail with $TiCl_4$ as a precursor, it was found out that the surface roughening has its origin in agglomerates formed during the early stages of the film growth.[6] The agglomeration was concluded to be driven by the film–substrate interface energy. Even though no unambiguous explanation could be given for the mechanism leading to the agglomeration while still preserving the self-control of the film growth, surface migration of hydroxyl groups, and gas-phase migration of volatile intermediates, *e.g.*, $Ti(OH)_2Cl_2$, were considered as the most feasible ones.[6] If gas-phase migration of analogous transient intermediating species, *e.g.*, $Ti(OH)_x(OCH_2CH_3)_{4-x}$, were the dominant mechanism in respect of the roughening observed in the present study, one could understand the roughness reducing effect of the self-decomposition in terms of a prevented migration of those TiO_2 units which were incorporated *via* the self-decomposition.

Another potential explanation for the rough surface of a film grown in the exchange reaction dominated region is that the exchange reactions may be structure sensitive,

---

(19) Ritala, M.; Leskelä, M. *Appl. Surf. Sci.* **1994**, *75*, 333.

i.e., they may be favored by crystal planes providing suitable coordination environment. Once such planes are formed, TiO_2 will grow faster upon them than upon the other surface leading to an uneven surface. Finally, also the less crystalline structure of the film grown using 3.0-s reactant pulses may explain why it is smoother than the film grown with 1.0-s pulses (Figure 5).

Within the accuracy limits of RBS the films were stoichiometric TiO_2. The atomic densities obtained by RBS were converted to geometrical thicknesses using the density of anatase. This gave values in good agreement with those obtained by fitting the transmittance spectra indicating that the films had high densities.

The film grown at 300 °C was analyzed for carbon residues with XPS and depth profiling by argon ion sputtering. Some carbon was detected at the outermost surface, but its content decreased below the detection limit of XPS already after a gentle sputtering. Thus, it was concluded that the exchange reaction between $Ti(OCH_2CH_3)_4$ and water was complete and the carbon detected at the surface was caused by postdeposition contamination. For a comparison, it is worth noting that carbon content in TiO_2 film grown by the chemical vapor deposition (CVD) technique from $Ti(OCH_2CH_3)_4$ at 308 °C was high enough, *i.e.*, on the order of 5 at. %, to be detected in Auger depth profiles.[20] The carbon contamination was found to be effectively decreased both by elevating the deposition temperature and by increasing the oxygen content in the gas phase.

Hydrogen profiles obtained from NRA measurements were similar to those found earlier with $TiCl_4$ and $Ti(OCH(CH_3)_2)_4$ as precursors.[4,7] In the bulk of the films the hydrogen contents were low, below 0.3 at. %, while at both film interfaces higher amounts were detected. Ottermann *et al.*[21] have shown that low hydrogen contents in TiO_2 films correlate with high refractive indices which, in turn, are known to correlate with high film densities.[22,23] Indeed, high refractive indices, on the order of 2.5, were evaluated from transmittance spectra for the films deposited at or above 250 °C.

Films were etched by 70% H_2SO_4 at 120 °C. The etching rate obtained, 10 nm/h, is of the same magnitude as those measured for the other ALE grown TiO_2 films.[4,7] By contrast, it has been reported that films grown from $Ti(OCH(CH_3)_2)_4$ and $Ti(OCH(CH_3)_2)_2(acac)_2$ (acac = acetylacetonato) by CVD were easily etched by 70% H_2SO_4.[24]

Postannealing at 500 °C for 2 h did not bring about any notable changes in film thicknesses or refractive indices. Also the XRD patterns remained essentially unchanged. Similar stability was also observed for the films grown by ALE using $Ti(OCH(CH_3)_2)_4$ as a precursor.[7] On the other hand, TiO_2 films grown by CVD have shown substantial crystallization during comparable postannealing procedures.[22,25] In these studies the simultaneously occurring thickness shrinkages and increases in refractive indices revealed that the crystallization was accompanied by a notable densification. Therefore, the resistance of the ALE films against crystallization can be related to their high densities already in the as-deposited forms.

Table 1. Estimated Molecular Radii Together with the Observed and Theoretically Calculated (See Text) Growth Rates for the Titanium Precursors Studied

Ti precursor	r(Ti–precursor)[a] (Å)	obs v_g (Å/cycle)	calc v_g (Å/cycle)	calc v_g/obs v_g
$TiCl_4$	3.2	0.56	0.99	1.8
$Ti(OCH_2CH_3)_4$	3.9	0.35[b]	0.67	1.9
$Ti(OCH(CH_3)_2)_4$	4.4	0.30	0.52	1.7

[a] Evalulated from the liquid densities assuming a close packing of spherical molecules. [b] Estimated contribution of the exchange reaction.

Comparison of the Titanium Precursors. Table 1 presents the highest ALE growth rates observed together with the calculated ones for the three titanium precursors studied. The experimental value given for $Ti(OCH_2CH_3)_4$ was estimated as described above. The theoretical calculations were based on the following assumptions: (i) The growth plane of the film is the (101) plane of anatase. (ii) The titanium precursor molecules are spheres whose radii (r(Ti–precursor) in Table 1) were calculated from the densities of the corresponding liquids[26] assuming close-packed arrangement. (iii) The area covered by an adsorbed precursor is a circle with a radius equivalent to the radius of the corresponding molecule. (iv) A close-packed arrangement prevails within the chemisorption layer, *i.e.*, 91% of the surface is covered by the precursors. According to these postulations the theoretical growth rates are obtained from the following equation:

$$v_g = 0.91[A(\mathrm{TiO_2})_{(101)}/\pi r(\text{Ti–precursor})^2]d_{(101)} \qquad (5)$$

where $A(TiO_2)_{(101)}$ (=10 Å^2) is the area per each TiO_2 unit projected on the (101) plane and $d_{(101)}$ (=3.5 Å) is the interlayer spacing. $A(TiO_2)_{(101)}/\pi r(\text{Ti–precursor})^2$ represents the density of titanium atoms within the chemisorption layer in relation to their density in a complete anatase (101) layer.

Table 1 reveals an evident inverse relationship between the growth rates and the sizes of the precursor molecules. However, in every case the theoretical growth rates are almost twice as high as the observed ones. There are several feasible explanations for these differences. First of all, the molecular sizes used in the theoretical calculations were only approximate. Moreover, if the growth mechanism involves exchange reactions between the Ti-precursor and surface hydroxyls, the effective size of the resulting Ti–species will differ somewhat from that assumed for a chemisorbed precursor. It was also supposed that a closed-packed arrangement prevails within the chemisorption layer which, however, underestimates interactions between the chemisorbed species and the surface atoms. These interactions are likely to be strong enough to localize the adsorption and, therefore, to prevent the close-packed arrangement. Furthermore, the species liberated in exchange reactions or in possible dissociative chemisorption processes can adsorb onto the surface and, thus, block out adsorption sites from the precursors. Finally, also the agglomeration has to be taken into account since it has been speculated that the migration mechanism leading to the agglomeration might involve volatile intermediates which could also lead to a loss of titanium-containing species from the chemisorption layer.[6,7]

---

(20) Won, T.-K.; Yoon, S. G.; Kim, H.-G. *J. Electrochem. Soc.* **1992**, *139*, 3284.

(21) Ottermann, C. R.; Bange, K.; Wagner, W.; Laube, M.; Rauch, F. *Surf. Interface Anal.* **1992**, *19*, 435.

(22) Frenck, H. J.; Kulisch, W.; Kuhr, M.; Kassing, R. *Thin Solid Films* **1991**, *201*, 327.

(23) Guenther, K. H. *Appl. Opt.* **1984**, *23*, 3612.

(24) Balog, M.; Schieber, M.; Patai, S.; Michman, M. *J. Cryst. Growth* **1972**, *17*, 298.

(25) Fitzgibbons, E. T.; Sladek, K. J.; Hartwig, W. H. *J. Electrochem. Soc.* **1972**, *119*, 735.

(26) *CRC Handbook of Chemistry and Physics*, 62nd ed.; CRC Press: Boca Raton, FL, 1981; pp B-159, C-688.

The films deposited from $TiCl_4$ were characterized by a sharp thickness profile at the leading edge of the substrate whereas those obtained from the alkoxides were slightly profiled over the whole substrate. In case of $TiCl_4$ the thickness nonuniformity was related to the CVD-like growth arising from desorption of one reactant from walls upstream of the substrate during the pulse sequence of the other reactant.[4] Even though the desorbed species were readily exhausted from the gas phase after the crossing point of the reactant flow routes, the location of this point only about 1 cm ahead of the substrate led to an overlap between the tail of the CVD growth region and the fore edge of the substrate. In case of the alkoxides the situation is more complicated since also the decomposition processes may have a contribution to the thickness nonuniformity.

The observation that $Ti(OCH_2CH_3)_4$ is thermally less stable than $Ti(OCH(CH_3)_2)_4$ is somewhat surprising since the thermal stability of zirconium alkoxides has been observed to decrease in the order of primary > secondary > tertiary.[8] Moreover, Kurtz and Gordon[27] noticed that for equivalent, maximum CVD growth rates a higher decomposition temperature was needed with $Ti(OCH_2CH_3)_4$ (480 °C) than with $Ti(OCH(CH_3)_2)_4$ (430 °C). A feasible explanation for these contradictory results can be found from the activation energies of the decomposition processes. In contrast to an activation energy of 28 kJ mol^{-1} given for $Ti(OCH_2CH_3)_4$[16] higher values ranging from 35 to 150 kJ mol^{-1} have been reported for the decomposition of $Ti(OCH(CH_3)_2)_4$.[17,28,29] Thus, the decomposition of $Ti(OCH(CH_3)_2)_4$ is more strongly temperature dependent than the decomposition of $Ti(OCH_2CH_3)_4$ which can explain the reversed orders of thermal stabilities observed, especially when it is kept in mind that essentially different decomposition rates, *i.e.*, different decomposition temperatures, were exploited in judging the thermal stabilities. Furthermore, the dominant decomposition mechanisms in these two studies are not necessarily the same since reactive scattering measurements have shown that different decomposition products are formed from $Ti(OCH(CH_3)_2)_4$ below and above 400 °C.[29]

The different temperature dependencies of the two decomposition processes can be clearly seen from Figure 3. In contrast to the smooth behavior exhibited by $Ti(OCH_2CH_3)_4$ an abrupt rise in the growth rate was observed with $Ti(OCH(CH_3)_2)_4$ at 350 °C. This rise was accompanied by a drastic deterioration of the film thickness uniformity[7] whereas the films obtained from $Ti(OCH_2CH_3)_4$ had relatively good uniformities even when grown at 350 °C (Figure 4).

At 250 °C, $Ti(OCH(CH_3)_2)_4$ was found to react with water more readily than $Ti(OCH_2CH_3)_4$ since 0.6-s pulse sequences were long enough to realize the growth rate saturation with $Ti(OCH(CH_3)_2)_4$,[7] whereas 1.5-s pulses were needed to reach the turning point with $Ti(OCH_2CH_3)_4$. The same order of sensitivity toward hydrolysis has been found also in sol–gel processes where it has been related to the coordination environment of titanium.[30] When coordinated to bulky alkoxide groups, titanium atoms are only weakly oligomerized and have their average coordination numbers close to four which makes them more prone to nucleophilic attack of water than titanium atoms in alkoxides with less bulky ligands where their coordination numbers are higher due to oligomerization. Apparently, the reaction rates on the surfaces of the growing ALE films are determined in a similar manner.

The crystallinity of the films grown in the present study supports our earlier speculation that the more crystalline structure of the films deposited from $Ti(OCH(CH_3)_2)_4$ relative to those obtained from $TiCl_4$ was due to the ordering effect of the bridged alkoxide groups.[7] Also the detrimental effect of the $Ti(OCH_2CH_3)_4$ decomposition on the film crystallinity can be regarded as further evidence for this hypothesis. Unfortunately the decomposition of $Ti(OCH_2CH_3)_4$ makes the mutual comparison of the alkoxides difficult, and thus no reliable correlation of the film crystallinity to the bridging property of the ligand can be made. At a deposition temperature of 250 °C, where the XRD reflections from the films grown from $Ti(OCH_2CH_3)_4$ were most intense, the films obtained from the two alkoxides possessed comparable crystallinities. However, when the deposition temperature was elevated, the crystallinity of the films deposited from $Ti(OCH_2CH_3)_4$ was reduced (Figure 4) while in the case of $Ti(OCH(CH_3)_2)_4$ 3-fold increases in the XRD peak intensities were observed when the temperature was increased from 250 to 325 °C.

Despite the differences discussed above, all three titanium precursors resulted in films with similar properties, *i.e.*, high refractive indices, low hydrogen contents in the bulks of the films, close agreement of thickness values obtained from RBS and transmittance measurements, as well as high resistance against etching with H_2SO_4, which altogether indicate that the films were of high densities. Moreover, in every case no ligand residues from the titanium precursors could be detected by RBS (chlorine) or by XPS (carbon). On the other hand, also the surface roughening was common for these processes.

Conclusions

ALE growth of TiO_2 thin films from titanium ethoxide and water as reactants was studied. No totally self-controlled growth could be achieved because of the thermal decomposition of the titanium precursor. Nevertheless, the characteristic features of the ALE technique were still preserved: the process was highly reproducible, providing an accurate thickness control and the resulting films possessed good uniformities and high densities. No carbon residues were found from the films with XPS.

To examine the effects of the titanium precursors on growth rates and film properties, titanium ethoxide was compared with the other titanium precursors studied, *i.e.*, $TiCl_4$ and titanium isopropoxide. It was found out that the growth rates were inversely related to molecular sizes of the precursors used. Despite the lower deposition temperatures, the films grown from the alkoxides were more crystalline than those deposited from $TiCl_4$ which was correlated to an ordering effect of the alkoxide ligands bridged between titanium cations on the surface of the growing film. The mutual comparison of the alkoxides is, however, difficult due to the crystallinity reducing effect of the $Ti(OCH_2CH_3)_4$ self-decomposition.

Acknowledgment. The authors are indebted to Mrs. L.-S. Johansson for the XPS measurements and to Mr. Pekka Haussalo for the NRA experiments. Prof. L. Niinistö and Mr. T. Prohaska are acknowledged for the AFM studies. This work was supported in part by the Academy of Finland and Technology Development Centre (TEKES), Helsinki, Finland.

---

(27) Kurtz, S. R.; Gordon, R. G. *Thin Solid Films* **1987**, *147*, 167.

(28) Yokozawa, M.; Iwasa, H.; Teramoto, I. *Jpn. J. Appl. Phys.* **1968**, *7*, 96.

(29) Wu, Y.-M.; Bradley, D. C.; Nix, R. M. *Appl. Surf. Sci.* **1993**, *64*, 21.

(30) Livage, J.; Sanchez, C. *J. Non-Cryst. Solids.* **1992**, *145*, 11.