Titanium Isopropoxide as a Precursor in Atomic Layer Epitaxy of Titanium Dioxide Thin Films

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Atomic layer epitaxy (ALE) deposition of titanium dioxide thin films using titanium isopropoxide and water as precursors was studied. The deposition temperature was limited to below 350 °C by the thermal decomposition of the alkoxide. Films were studied by means of spectrophotometry, XRD, RBS, NRA, SEM, and AFM. A comparison with the ALE process using titanium tetrachloride as a titanium precursor is being carried out.

Introduction

Metal alkoxides[1-3] have become widely used precursors in chemical vapor deposition (CVD) of oxide thin films. This is due to their excellent properties, especially volatility and suitable thermal stability for CVD process, *viz.*, they are completely vaporized but they decompose into oxides and volatile byproducts at relatively low temperatures. As a result of the low deposition temperature, a wide range of substrate materials can be used. Furthermore, the deposition of oxide films can be performed at even lower temperatures by hydrolysis of the alkoxides. Metal alkoxides are easy to prepare and purify and being intrinsically noncorrosive they can be stored almost indefinitely when kept in a dry atmosphere. A number of metal alkoxides having industrial applications are commercially available with high purities and relatively low prices. Compared with metal halides, the traditional CVD precursors for oxide films, alkoxides provide a wider range of volatile metal compounds and hence a larger variety of oxides to be deposited. Additionally, the problems of corrosive byproducts causing substrate and reactor damages in halide processes are avoided.

Despite of their success as CVD precursors metal alkoxides are seldom used in a related method, atomic layer epitaxy (ALE).[4-6] In ALE reactants, elements or compounds, are pulsed alternately on the substrate and the reactor is purged with an inert gas between the reactant pulses. When the deposition conditions, especially the substrate temperature, are properly adjusted only the chemisorbed species are retained on the substrate during the purge sequence and the film growth takes place layer by layer. However, due to the steric hindrance of bulky reactant molecules the number of chemisorbed species is often too small for a formation of a complete crystal layer during one cycle and, consequently, the growth rate is less than one monolayer per cycle.[4] Nevertheless, the film thickness is still controlled simply by the number of reaction cycles used and the growth is said to be self-controlled or self-limited.

The most likely reason for the limited number of ALE studies with alkoxide precursors is the risk that the self control of the film growth becomes destroyed by the thermal decomposition of the alkoxide. The first reports about alkoxides as precursors in ALE process were concerned with a deposition of Al_2O_3 films.[7] These experiments proved that self-controlled growth can be achieved at temperatures below the point where the direct decomposition of the alkoxide becomes dominant. For example, with aluminum ethoxide the growth rate was independent of the deposition temperature and the durations of pulse and purge sequences at 350-450 °C. Above 450 °C the growth rate increased as a consequence of the self decomposition, i.e. the growth took place by a CVD mode. Recently, Döring *et al.*[8] have used the ALE process to grow TiO_2 films from titanium isopropoxide and water. On the basis of the low deposition temperature, $T \leq 150$ °C, the contribution of the thermal decomposition of the alkoxide was excluded.

Titanium dioxide thin films have a number of applications in optics and electronics because of its excellent properties, *viz.*, chemical and physical stability, high refractive index, good transmission in vis and NIR regions, and high dielectric constant. In our previous work, TiO_2 films were grown by ALE using $TiCl_4$ and water as reactants.[9] The problems with $TiCl_4$ comprise corrosive byproducts and possible chlorine residues in the film.

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Table I. Volatilities and Molecular Complexities, *i.e.*, Degree of Oligomerization (n in $(Ti(OR)_4)_n$), of Some Titanium Alkoxides[1]

R in $Ti(OR)_4$	Boiling point (°C/mmHg)	n in $(Ti(OR)_4)_n$
C_2H_5	103/0.1 138.3/5.0	2.4
$(CH_3)_2CH$	49/0.1 91.3/5.0	1.4
$(CH_3)_3C$	93.8/5.0	1.0
$(C_2H_5)(CH_3)_2C$	142.7/5.0	1.0
$(C_2H_5)_2CH$	112/0.1	1.0

Furthermore, the presence of chlorine may generate volatile species which can be responsible for the observed agglomeration during the film growth.[10] In this paper alkoxides are considered as alternative titanium precursors. To start with, the properties of alkoxides are briefly examined from the ALE process point of view.

Titanium Precursor for the ALE Process. The main items to be considered when selecting an alkoxide precursor for the ALE process are vapor pressure and resistance against thermal self-decomposition. The volatilities of alkoxides with lower alkyl groups are effected by the oligomerization, *i.e.*, the formation of polymeric species $(Ti(OR)_4)_n$.[1-3] Oligomerization is driven by the tendency of the metal to saturate its coordination number and facilitated by the property of the alkoxide group to act, in addition to as a terminal one, as a bridging ligand when bonded through its oxygen atom to two or three metal cations. Oligomerization decreases volatility relative to the monomer because either extra energy is needed to break bridging bonds or, if these bridging bonds are preserved in the gas phase, intermolecular forces are stronger due to the greater size of the oligomer as compared to the monomer. The oligomerization is sterically prevented by bulky alkyl groups; especially *tert*-alkyls are effective to prevent oligomerization and promote higher volatility. However, as the carbon chain of the ligand increases the intermolecular forces between the alkyl groups increase lowering volatility. As a consequence, titanium isopropoxide ($Ti(OCH(CH_3)_2)_4$) has the highest vapor pressure of titanium alkoxides (Table I)[1] which is presumably the reason for $Ti(OCH(CH_3)_2)_4$ being the most widely used precursor in CVD growth of TiO_2.

The demand of reasonable volatility of the precursors is common for CVD and ALE, but these processes differ from each other in respect to the demands concerning thermal stabilities of the reactants. In CVD the thermal stability is usually only needed during the transportation to avoid premature gas-phase reactions. In ALE the precursors must be stable enough not to decompose by themselves even on the heated substrate surface, otherwise the self-controlled growth is lost.

Among alkoxides the effect of the ligand on the thermal stability has been studied most thoroughly for zirconium alkoxides.[1,11,12] Their stability decreases in the order primary > secondary > tertiary. On the basis of the general similarity of the properties of titanium and zirconium alkoxides and the observation that titanium ethoxide does decompose at about 50 °C higher temperatures than titanium isopropoxide,[13] the same stability order is likely to be valid for titanium alkoxides as well. The easy decomposition of zirconium *tert*-butoxide was related to a chain reaction mechanism where the alkoxide is hydrolyzed by water produced in the dehydration of the tertiary alcohol.[1,2,11,12] The process was presumed to be initiated by the reaction of the alkoxide with water adsorbed on surfaces in contact with the gas phase. Surfaces, especially glass surfaces, are also likely to catalyze the dehydration of the tertiary alcohol.[2] Once initiated, the process propagates fast because one alcohol molecule produces one water molecule which in turn regenerates two alcohol molecules in hydrolysis of the alkoxide. Since the dehydration is less facile for secondary and especially for primary alcohols they are more stable and their thermolysis is expected to take place by a different mechanism.[12]

Some information about the decomposition mechanism of $Ti(OCH(CH_3)_2)_4$ is obtained from the work of Siefering and Griffin,[14,15] who have studied the kinetics of the CVD growth of TiO_2 by thermolysis of $Ti(OCH(CH_3)_2)_4$. They proposed a three step mechanism for the film growth: (i) bimolecular collisional activation of $Ti(OCH(CH_3)_2)_4$ in the gas phase, (ii) adsorption of the activated species and (iii) decomposition of the adsorbed species. With low $Ti(OCH(CH_3)_2)_4$ vapor pressures and/or at high substrate temperatures the growth rate followed second-order kinetics with respect to $Ti(OCH(CH_3)_2)_4$ when no carrier gas was used,[14] whereas with an excess nitrogen carrier first-order kinetics were observed.[15] The rate limiting step at these conditions was interpreted to be the collisional activation of $Ti(OCH(CH_3)_2)_4$ with either another $Ti(OCH(CH_3)_2)_4$ molecule or with nitrogen molecule. The form of the activated species could not be determined, but on the basis of a temperature-programmed desorption study[14] it was suspected that the activation might involve a loss of one or more alkoxide groups in the form of acetone. At low temperatures and with high $Ti(OCH(CH_3)_2)_4$ pressures, the growth rate showed zero-order kinetics attributed to surface reaction limited process.

Temperature-programmed desorption study of $Ti(OCH(CH_3)_2)_4$ on oxygen predosed copper has shown that the adsorbed species decomposes in two stages producing acetone and hydrogen at 177 °C and propene and hydrogen at 347 °C.[14] The latter temperature is likely to be the more important one for the ALE process since it can be expected that only after a total decomposition of the precursor molecule the self-controlled film growth is lost. The partial decomposition could lead to a chemisorbed layer which would be bonded to the surface *via* Ti atoms while the remaining alkoxide ligands pointing upward could prevent the formation of another tightly bonded adsorption layer and, subsequently, only the chemisorbed layer would be retained on the surface during the purging sequence.

Recently, Wu *et al.*[16] have studied $Ti(OCH(CH_3)_2)_4$ by means of temperature-programmed reaction spectroscopy experiments which were, in principle, comparable to the TPD studies of Siefering and Griffin.[14] However, essentially divergent results were obtained which were attributed to the different substrate materials used.[16] Wu *et al.* carried out their experiments using TiO_2 films as a

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substrate, whereas oxygen predosed copper was exploited by Siefering and Griffin. Moreover, Wu *et al.* used smaller $Ti(OCH(CH_3)_2)_4$ doses (1–10 langmuirs) than Siefering and Griffin (10–1000 langmuirs). The results of Wu *et al.* did agree with those of Siefering and Griffin about the onset temperature (180 °C) of the decomposition. However, despite the lower heating rate, no separate decomposition stages were distinguished. Furthermore, propene was the main decomposition product at all temperatures including also the onset temperature where Siefering and Griffin detected acetone as a dominant species.

Wu *et al.*[16] carried out also reactive scattering measurements by introducing a constant $Ti(OCH(CH_3)_2)_4$ flux onto TiO_2 film in UHV and monitoring the scattered species as a function of temperature. The main decomposition products below 400 °C were isopropyl alcohol, and acetone, whereas at higher temperatures propene and water were the dominant species. Besides the change in temperature also the surface coverage of the adsorbed species was considered to be responsible for the change in decomposition products. Since the surface coverage decreased with increasing temperature, it was suggested that the mechanism involving the formation of isopropanol and acetone would be favored by high coverages whereas the formation of propene and water would be enhanced at lower coverages.[16]

$Ti(OCH(CH_3)_2)_4$ was chosen as the titanium precursor in this work even though it is not as stable as titanium ethoxide.[13] This choice was favored by the high vapor pressure of $Ti(OCH(CH_3)_2)_4$. The titanium *tert*-butoxide was rejected despite of its high vapor pressure (Table I) because, on the basis of above discussion about zirconium alkoxides, it is assumed to be facile to thermal decomposition.

Oxygen Precursor. A careful choice of the other presurcor is naturally essential for a successful ALE process. Because alkoxides contain oxygen as a constituent, no additional oxygen source is necessary in the CVD growth of oxides and in some cases TiO_2 has been deposited by simply decomposing $Ti(OCH(CH_3)_2)_4$ in an inert carrier gas.[13,15,17] However, the more common way is to decompose $Ti(OCH(CH_3)_2)_4$ in the presence of oxygen.[17–22] Also plasma assisted processes[23,24] and hydrolysis reaction[25–27] have been used. Because without any additional energy source, *e.g.*, laser or plasma, the ALE process can not be carried out by decomposing a single precursor, the other precursor must be reactive enough to facilitate film growth at temperatures where the alkoxide does not pyrolytically decompose. As a result of the facile hydrolysis of alkoxides, water is a natural choice to be used as another precursor.

The effect of oxygen source on CVD film properties was pointed out by Fuyuki *et al.*,[28] who studied TiO_2 films grown by decomposing $Ti(OCH(CH_3)_2)_4$ in the presence of oxygen and a small, variable amount of water. The most important properties of the films, *viz.*, refractive index, resistance against etching, dielectric constant, resistivity and breakdown field, were improved when the amount of water was increased from 0 to 300 ppm. These improvements were related to the enhancement of the Ti–O bond formation in the presence of water. Because the effects of even small variations in the amount of water were remarkable Fuyuki *et al.* concluded that in order to deposit films with reproducible properties the accurate control of the water content is needed. However, most of the properties were not saturated in the range studied. The amount of water was not increased above 300 ppm because the growth rate decreased remarkably with increasing water content due to the gas-phase reactions prior to the substrate. It seems that the best film quality could be obtained by increasing the water content but this sets high demands on the hydrodynamic design of the reactor in order to avoid gas phase reactions and to achieve a good film thickness uniformity. ALE is an effective method to circumvent these problems since the gas-phase reactions are avoided by the pulsing of the reactants and the thickness uniformity is an inherent result of the self-controlled growth.

Experimental Section

The film deposition was carried out using a commercial flow type reactor F-120 (Microchemistry Ltd., Espoo Finland).[6] $Ti(OCH(CH_3)_2)_4$ liquid (97% purity, Aldrich) was evaporated from an open boat at 40 or 50 °C. The corresponding equilibrium vapor pressures of $Ti(OCH(CH_3)_2)_4$ were calculated from the expression derived by Siefering and Griffin[15] to be 0.4 and 0.9 Torr, respectively. Nitrogen was led over the boat to carry the reactant vapor into the heated reaction zone. An external water reservoir held at 20 °C was connected to the cold end of the reactor through a capillary and a needle valve. From the cold end of the reactor water vapor was transported further by nitrogen. Total pressure of the reactor was on the order of 8 Torr. Pulse and purge times were varied from 0.2 to 0.8 s and from 0.5 to 1.0 s, respectively. Substrates used were 5×5 cm^2 soda lime glasses.

Film thicknesses and refractive indexes were determined by fitting measured transmittance spectra exploiting the matrix method[29] in the calculations. The transmittance spectra covering wavelengths from 380 to 1100 nm were measured with 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.[30] Crystal structure and crystallite orientation were determined with a Philips powder X-ray diffractometer MPD 1880 using Cu Kα radiation. Film morphology was characterized with a JEOL JSEM-820 scanning electron microscope and a Nanoscope II atomic force microscope (AFM). Hydrogen profiling was carried out 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.[31]

Results and Discussion

Self-Limited Growth. Figure 1 depicts the growth rate as a function of temperature. It can be seen that a

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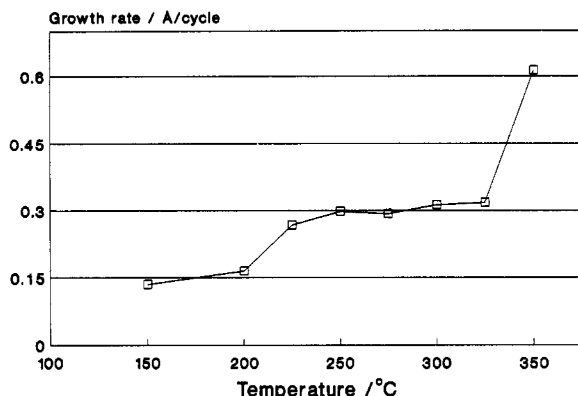

Figure 1. Temperature dependence of the growth rate for films grown using 0.6-s pulses and 0.5-s purging. The data were evaluated at 35 mm from the leading edges of the substrates.

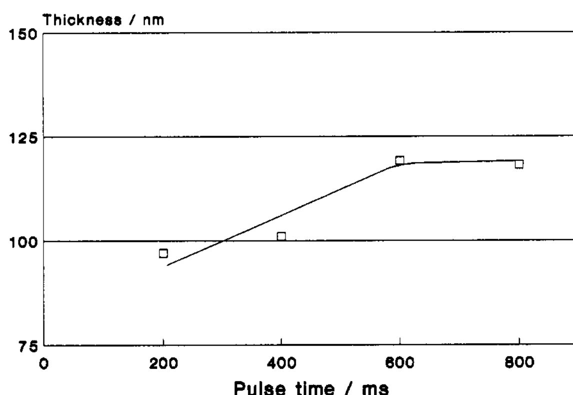

Figure 2. Thicknesses of films grown by 4000 cycles at 250 °C as a function of the pulse duration.

temperature-independent growth rate of 0.30 Å/cycle is obtained between 250 and 325 °C. To verify that the growth mechanism is really self-controlled instead of mass transport limited decomposition of the alkoxide, the pulse duration was varied at 250 °C (Figure 2). The saturation of the growth rate at a constant level when the pulse time is 0.6 s or above confirms that the growth is self-controlled. The chemisorbed layers were stable since the doubling of the purge sequence from 0.5 to 1.0 s had no effect on the growth rate at 250 °C. Below 250 °C the film growth is controlled most likely by kinetics of surface processes (to be discussed below).

When the growth temperature is raised to 350 °C, the thermal decomposition of $Ti(OCH(CH_3)_2)_4$ becomes dominant resulting in a heavily profiled film as judged by means of interference colors which change rapidly in the flow direction. It is worth noting that the temperature where the decomposition becomes dominant coincides well with the results of Siefering and Griffin,[14] who reported that the latter step of the decomposition of adsorbed $Ti(OCH(CH_3)_2)_4$ takes place at 347 °C.

To study the possible contribution of the decomposition of $Ti(OCH(CH_3)_2)_4$ to the film growth at 250 °C, only $Ti(OCH(CH_3)_2)_4$ and nitrogen were alternately pulsed into the reactor. After 8000 cycles a film with an atomic density of 50×10^{15} cm^{-2} corresponding to a thickness of 6 nm was observed by RBS. According to the calculations based on the water exposure needed to achieve a saturated growth in the ALE process the effect of water and oxygen residuals

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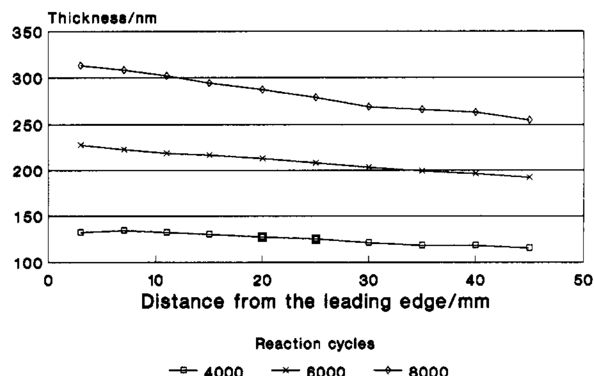

Figure 3. Thickness profiles of films grown at 250 °C by 4000, 6000, and 8000 cycles.

seems to be insignificant for the observed growth which is, therefore, related to the thermal decomposition of $Ti(OCH(CH_3)_2)_4$. Nevertheless, since the corresponding growth rate (0.008 Å/cycle) is only about 3% of the observed ALE growth rate, it can be concluded that the main mechanism for the film deposition in the ALE process is the self-controlled reaction between $Ti(OCH(CH_3)_2)_4$ and water.

It should be kept in mind that the above experiment concerning the thermal stability of the alkoxide is not necessarily relevant to the ALE process since the surface of the growing TiO_2 film may catalyze the decomposition of $Ti(OCH(CH_3)_2)_4$ more effectively than the surface of the glass substrate. Wadayama *et al.*[18] have observed that when $Ti(OCH(CH_3)_2)_4$ is used as a precursor in the CVD growth of TiO_2 the deposition rate is initially small but increases as the substrate—a gold film—becomes oxide covered. They attributed this change to sticking probabilities and nucleation rates which depend strongly on the nature of the substrate surface. Even though in their study the difference in the chemical properties between the substrate and film surfaces were more remarkable than in our case, a similar effect is possible also in the present study.

Figure 3 depicts film thicknesses as a function of the distance from the leading edge of the substrate for films grown at 250 °C using different numbers of reaction cycles. The film thicknesses decrease slightly in the direction of the gas flow. There are two possible reasons for this thickness nonuniformity. First, it was observed that some film growth took place even when only $Ti(OCH(CH_3)_2)_4$ and nitrogen were alternately pulsed into the reactor. However, the thickness of the resulting film was only about 10% of the thickness nonuniformity in the film grown by corresponding number (8000) of ALE cycles (Figure 3). Additionally, with such a low deposition rate the design of our reactor[6] should provide sufficient $Ti(OCH(CH_3)_2)_4$ flux to maintain constant surface concentration on the substrate. Thus, the process should be surface reaction controlled leading to a uniform film growth in contrast to the observed nonuniform one. On the other hand, the potential catalytic effect of the TiO_2 film surface, discussed above, may have a contribution also to the thickness nonuniformity. If the thermal decomposition were the origin of the thickness nonuniformity the lengthening of the pulse time should result in a stronger profile. However, no remarkable differences were observed between films grown using 0.6- and 0.8-s pulses.

The more feasible reason for the thickness nonuniformity is the weak CVD-like growth which has been observed

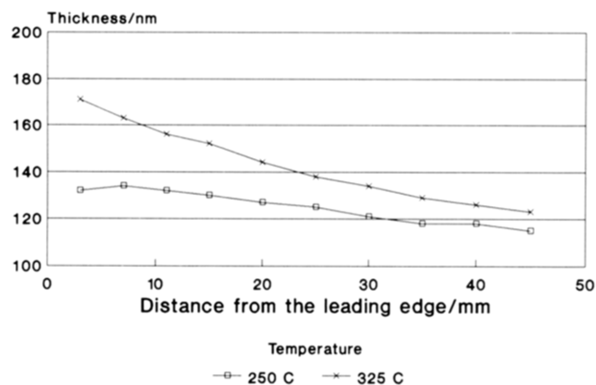

Figure 4. Thickness profiles of films grown by 4000 cycles at 250 and 325 °C.

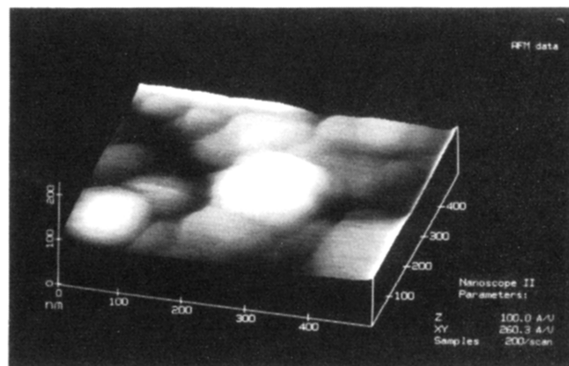

Figure 5. AFM image of film grown at 300 °C by 4000 cycles (scan area 500 × 500 nm^2; z scale 200 nm).

to take place as a consequence of desorption of one precursor from the walls upstream of the substrate during the pulse sequence of the other reactant.[9] Even though the desorbed species are rapidly 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 provides that in our reactor the tail of the CVD growth region overlaps with the substrate. In the previous study[9] where $TiCl_4$ was used as a titanium precursor, the CVD growth resulted in a sharp profile extending no more than 20 mm from the leading edge of the substrate after which the film thickness achieved a constant value whereas in the present study no sharp profile region could be observed. This difference can be attributed to the less facile hydrolysis of $Ti(OCH(CH_3)_2)_4$ relative to $TiCl_4$.

With the existing data the prevailing mechanism in respect of the thickness nonuniformity cannot be distinguished. Therefore, additional experiments carried out in a reactor where the crossing point of the reactant flow routes would be located far ahead of the substrate might be advantageous.

The thickness measurements for the growth rate determination (Figure 1) were carried out at about 35 mm from the leading edge of the substrate in order to minimize the effect of the thickness nonuniformity. Consequently, even though the growth rate seems to be stabilized between 250 and 325 °C thickness nonuniformity increases as the growth temperature increases (Figure 4) which is an expected result, no matter which one of the mechanisms discussed above causes the nonuniformity. At 350 °C where the self-decomposition becomes dominant, the thickness nonuniformity is much more severe than in any of the films grown at lower temperatures.

The observed growth rate is only one-fifth of the rate obtained by Döring *et al.*[8] using principally the same process. However, the dissimilar experimental conditions, like substrate temperature, pulse and purge durations, reactant and total pressures and reactor geometry, make a direct comparison difficult. Especially the substrate temperature is assumed to be significant since Döring *et al.* carried out their experiments below 150 °C where the TiO_2 surface is likely to be hydroxylated and may even have some molecular water adsorbed on it whereas our results concerning the saturated growth rate were obtained above 225 °C where dehydroxylation processes[32] may essentially change the reactivity of the TiO_2 surface toward chemisorbing $Ti(OCH(CH_3)_2)_4$. Moreover, Döring *et al.* gave no explicit evidence about the self-control of the film growth, especially in respect of sufficient purging. Nevertheless, both studies showed that the ALE process provides a convenient way to control film thicknesses by the number of growth cycles used. Unfortunately the difficulties in achieving a complete thickness uniformity were also common for the both studies.

Film Structure and Properties. No structural defects, like cracks, were observed by SEM. To get a closer look at the film surface, AFM was exploited. A nonplanar surface morphology shown in Figure 5 was observed. Numerical estimations about the surface roughness of this film with a nominal thickness of 120 nm were obtained from the standard deviation (5.5 nm) and the total range (30 nm) of the z values from scan area of 500 × 500 nm^2. For comparison, the corresponding values for the bare soda lime substrate were 0.7 and 5.3 nm. Similar surface structures were observed in our previous study[10] where the morphological development of TiO_2 films grown by the chloride process was followed by AFM. That study revealed that the rate of roughening was at its highest at the very early stages of the film growth when agglomerates were formed on the surface. As the growth proceeded these agglomerates grew both horizontally and vertically and finally coalesced. It was concluded that the agglomeration was driven by the film–substrate interface energy. Several possible mechanisms for the migration needed for agglomeration were suggested, *e.g.*, surface migration of hydroxyl groups and gas-phase migration of volatile intermediates, like $Ti(OH)_2Cl_2$. Same kind of arguments are likely to prevail in the present process as well.

XRD measurements revealed the presence of anatase phase (Figure 6). The (101) reflection was the most intense one in all the films. In addition to the (101) reflection only the (200) reflection with a relative intensity of about 10 was observed from films grown at 275 °C or above. For films with comparable thicknesses, *i.e.*, the same number of deposition cycles, the reflection intensities increased together with the deposition temperature but their ratio remained essentially the same. The intensities of the reflections from the film grown at 325 °C were 3-fold the intensities of the corresponding reflections from the film grown at 250 °C. Together with the weakness of the diffraction patterns this shows that the films consisted of mixtures of amorphous and anatase phases where the fraction of the anatase phase increased with increasing deposition temperature. As distinct from films grown at higher temperatures, films deposited at 250 °C had also a weak (211) reflection of anatase. When the film thickness was increased at 250 °C all the reflections were intensified. For films grown using 6000 and 8000 reaction cycles the

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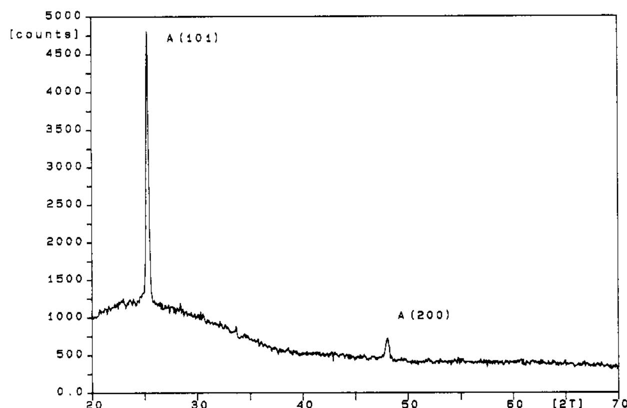

Figure 6. XRD pattern of film grown at 325 °C showing the anatase (A) (101) and (200) reflections.

(101) reflections were 1.7 and 2.1 times more intense than the corresponding reflection from the film deposited by 4000 cycles. The relative intensities of the (200) and (211) reflections were 10 and 5 (4000 cycles), 18 and 7 (6000 cycles), and 17 and 8 (8000 cycles), respectively.

Since the observed (101), (200), and (211) reflections are the most intense ones also in the anatase powder—though with somewhat different relative intensities (100, 35, and 20, respectively)[33]—one has to be careful when drawing any conclusions about the preferred orientation of the films. However, even though in the anatase powder both the (004) and (105) reflections have the same relative intensity as the (211) reflection[33] they were not observed from the films. Further evidence about preferred orientation is obtained from the absence of the (211) reflection from the films grown above 250 °C. Thus, it can be stated that the films grown above 250 °C are partially oriented. Furthermore, as the increase of the relative intensities of the minor peaks along with increasing film thicknesses shows, even at 250 °C the thinnest film seems to be oriented relative to the thicker ones.

The films obtained by Döring *et al.*[8] using an analogous process were amorphous which is most obviously a consequence of the low deposition temperatures used, $T \leq 150$ °C. Studies concerning the CVD growth of TiO_2 films by hydrolysis of $Ti(OCH(CH_3)_2)_4$ have shown crystallization behavior comparable to the present study. For example, Hovel[26] observed that the films grown on GaAs substrates transformed from an amorphous to a crystalline phase at a deposition temperature between 200 and 300 °C. Using a similar system as Hovel, Fitzgibbons *et al.*[27] obtained amorphous films at 150 °C. When annealed at 350 °C, these films transformed into a mixture of anatase and amorphous phases. Films annealed at 700 °C consisted of a anatase–rutile mixture, except for those on fused quartz substrates which retained the anatase structure even when annealed at 1000 °C. For the films deposited by a thermal decomposition of $Ti(OCH(CH_3)_2)_4$ the temperature of the amorphous to anatase transformation has varied widely from 200 to 550 °C.[18–20] Using plasma-enhanced decomposition of $Ti(OCH(CH_3)_2)_4$, Frenck *et al.*[23] obtained amorphous films in the whole substrate temperature range studied (150–310 °C). Also in that case annealing (400 °C) transformed amorphous films into a crystalline form.

Refractive indexes evaluated from transmittance measurements increased with increasing deposition temperature. Using 580 nm as a reference wavelength, the refractive indexes were 2.3 at 150 °C and 2.4 at 200 °C. The saturation level of 2.5 was reached at 225 °C. Comparison with the CVD process shows that the saturation of the refractive index is achieved at lower temperatures in the ALE process. Using the hydrolysis reaction, Hovel[26] obtained a strong temperature dependence for the refractive index which increased from 1.9 (100 °C) to 2.1 (200 °C) and further up to 2.4 (400 °C). Fitzgibbons *et al.*[27] observed that the refractive index is affected also by the post-annealing procedure. The increase of the refractive index from 2.0 for films grown at 150 °C up to 2.5 when annealed at 1000 °C was accompanied by a thickness shrinkage of as high as 35%. Also the films deposited by plasma-enhanced decomposition of $Ti(OCH(CH_3)_2)_4$ have shown similar behavior in respect of both the refractive index and the film thickness.[23] Thus, the increase of the refractive index is generally attributed to crystallization and densification of the film. Therefore refractive indexes can be employed to make estimations about film densities as evidenced by the strong correlation between the two quantities.[23] As a conclusion, the high refractive indexes indicate that TiO_2 films with a high density are obtained by the ALE process even at such a low temperature as 225 °C.

As was noted above, the post annealing has a considerable effect on CVD deposited TiO_2 films. Therefore, films grown by ALE at 250 °C were annealed at 480 °C for 60 min. The film densities seemed to be unaffected since no changes in either the refractive indexes or film thicknesses could be observed. Also the crystallinity of the films remained essentially the same though a slight increase of about 10% was observed in the XRD intensities. The only change resulting from further annealing for 6 h at 480 °C was an increase of 5% in the main peak intensity. Thus, even though it was concluded above that films grown at 250 °C consisted of a mixture of amorphous and anatase phases, no remarkable crystallization was induced by the annealing procedure known to be effective for CVD films. The most likely explanation for this is that the high density of the ALE films retards further ordering in contrast to the CVD films with a lower density.

Besides refractive indexes also hydrogen contents provide information about densities of oxide thin films.[34,35] The correlation between the hydrogen content and the film density lies in the facile adsorption of water on the oxide surfaces. Contrary to dense films where the adsorption takes place mainly on the outermost surfaces, water diffuses into porous films and adsorbs on the void limiting surfaces as well. Thus, films with different densities are readily distinguished by profiling them for hydrogen with NRA using the $^{1}H(^{15}N,\alpha\gamma)^{12}C$ resonant reaction. NRA measurements carried out showed that hydrogen contents in the bulks of the films were in the order of 0.3 at. %. As expected, considerably higher hydrogen contents were observed at the film surfaces. Also at the film–substrate interfaces the hydrogen contents were higher than in the film cores which was attributed to contamination of the substrate prior to film deposition.

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The observed hydrogen profiles were comparable to those of TiO_2 films deposited by ALE using $TiCl_4$ as a precursor.[9] Comparison with the results of Ottermann *et al.*[35] shows that among various sol–gel and physical vapor deposition techniques only ion plating and ion-assisted deposition resulted in TiO_2 films with hydrogen contents as low as those of the ALE-deposited films.

Since the hydrogen contents of the films grown from $Ti(OCH(CH_3)_2)_4$ did not differ from those of films grown from $TiCl_4$, it can also be concluded that no remarkable quantities of alkoxide residues were left in the films. However, there still remains a possibility that some elemental carbon may have been incorporated into the films.

Within the accuracy limits of the RBS films were stoichiometric TiO_2. The density of anatase was exploited to convert the atomic densities obtained from RBS measurements to geometrical thicknesses. This gave values close to those obtained from transmittance measurements which can be regarded as a further evidence about high film densities.

Film deposited at 250 °C was etched by 70% H_2SO_4 at 120 °C with a rate of 10 nm/h which is comparable to the etching rates (5–14 nm/h) obtained for the films grown by ALE at 250–500 °C using $TiCl_4$ as a titanium precursor.[9] On the other hand, Balog *et al.*[19] reported that films deposited by CVD from $Ti(OCH(CH_3)_2)_4$ and $Ti(OCH(CH_3)_2)_2(acac)_2$ (acac = acetylacetonato) were easily etched by 70% H_2SO_4. The etching temperature was not given, however.

Comparison with the Chloride Process. The most obvious difference between the alkoxide and chloride[9] processes is that whereas with $TiCl_4$ self-limited growth is achieved at all temperatures studied up to 600 °C the use of $Ti(OCH(CH_3)_2)_4$ is limited below 350 °C, and in order to achieve a reasonable thickness uniformity the temperature has to be kept below 300 °C.

At first glance one might expect that the low temperature in the alkoxide process would result in a poorer crystallinity relative to films deposited at higher temperatures in the chloride process. However, just the opposite behavior was observed. The films deposited from $Ti(OCH(CH_3)_2)$ were at least partially crystalline, whereas the films deposited from $TiCl_4$ onto the glass substrates were amorphous through the whole temperature range studied up to 600 °C; only on crystalline substrates crystalline films were obtained. This shows that the chemical properties of the precursors have a remarkable effect on the crystallinity of the films. An obvious chemical difference between these precursors is that the alkoxide itself contains Ti–O bonds whereas $TiCl_4$ does not. However, there are only four Ti–O bonds in the alkoxide and some of them are even likely to break during the growth process, whereas the coordination number of titanium in anatase is six. Thus, if crystalline TiO_2 is to be formed, titanium has to expand its coordination number to achieve the correct short-range order and, additionally, the resulting TiO_6 units have to get ordered coherently in the long-range scale. In ALE the expansion of the coordination number takes place on the surface of the growing film where the rearrangement of the atoms is retarded relative to a gas-phase nucleation. Thus, there has to be a mechanism which favors ordering on the surface more effectively in the alkoxide process than in the chloride process. The bridging property of the alkoxide group is likely to play a vital role. Even though the $Ti(OCH(CH_3)_2)_4$ molecules are only slightly oligomerized (n = 1.4) in liquid (Table I), the isopropoxide groups are expected to be effective to form bridges between titanium cations on the film surface because the steric hindrance is relaxed due to the reduced number of alkoxide groups per titanium cations. The bridging involves ordering, and thus the bridged surface layer can act as a constructive intermediate between an irregular adsorption layer and the crystalline film. Unfortunately no direct evidence about this mechanism is readily obtainable. One approach might be to use precursor which is more effectively oligomerized than $Ti(OCH(CH_3)_2)_4$, *e.g.*, titanium ethoxide (Table I).

Table II. Effects of the Pressure of $Ti(OCH(CH_3)_2)_4$ (p) and the Pulse Time on the Film Thickness at 250 °C (4000 Reaction Cycles)

p/Torr	pulse time/ms	thickness/nm
0.4	400	101
0.9	400	105
0.4	600	119

The pulse time needed to achieve a saturated growth rate is longer in the alkoxide process (0.6 s) than in the chloride process (0.2 s).[9] The exact pressure of $TiCl_4$ in the reactor is difficult to estimate because $TiCl_4$ was introduced into the reactor (total pressure 8 Torr) through a needle valve from an external reservoir where its pressure was 12 Torr. Nevertheless, it is obviously higher than the pressure of $Ti(OCH(CH_3)_2)_4$ (0.4 Torr), and one might attribute the different pulse times needed to the pressure difference. However, the effect of increasing the vapor pressure of $Ti(OCH(CH_3)_2)_4$ is negligible, whereas the elongation of the pulse time results in a considerably thicker film (Table II). As Figure 2 indicates, the pulse time of 0.6 s is sufficient to achieve a saturated growth rate. This shows that the achievement of the surface saturation is controlled mainly by surface processes taking place after the adsorption instead of mass transportation. Same kind of surface processes are likely to exist also in the $TiCl_4$ process because longer pulse times (0.4 s) were needed when the growth temperature was lowered from 500 to 300 °C. Thus, the pulse times required seem to be governed by thermally activated surface processes. Because the growth temperature must be kept below 350 °C when $Ti(OCH(CH_3)_2)_4$ is used as a precursor these processes are slower than in the chloride process carried out at 500 °C. Furthermore, as the crystallinity indicates, more ordering takes place on the surface in the alkoxide process.

One significant difference between these precursors is the achievable growth rate. The highest rate obtained with $TiCl_4$ is 0.56 Å/cycle, whereas with $Ti(OCH(CH_3)_2)_4$ the growth rate is only about 0.30 Å/cycle. Additionally, owing to the long pulse time needed with $Ti(OCH(CH_3)_2)_4$ the effective growth rate, *i.e.*, the growth rate per time unit, is even lower relative to the chloride process. Taking 0.5-s purge sequences for both processes the effective growth rate is 24 Å/min for $TiCl_4$ and 8 Å/min for $Ti(OCH(CH_3)_2)_4$.

The reason for the difference in the growth rate per cycle is most probably the larger size of $Ti(OCH(CH_3)_2)_4$ relative to $TiCl_4$. As the growth rate (v_g) is dependent on the number of titanium atoms in the chemisorbed layer, it is expected to be inversely related to the area (A) covered by the adsorbed precursor species. The sizes of the precursor molecules can be estimated from the densities of the corresponding liquids[36] assuming a close packed

arrangement of spherical molecules. This gives a radius of 3.2 Å for $TiCl_4$ and 4.4 Å for $Ti(OCH(CH_3)_2)_4$. It can be supposed that the space needed by the adsorbed species is a circle with a radius equivalent to the radius of the corresponding molecule. Thus the area needed is 32 $Å^2$ for $TiCl_4$ and 61 $Å^2$ for $Ti(OCH(CH_3)_2)_4$. Indeed, the expected inverse relationship between the maximum growth rate and the area per adsorbed species is confirmed: $v_g(TiCl_4)/v_g(Ti(OCH(CH_3)_2)_4) = [A(TiCl_4)/A(Ti(OCH(CH_3)_2)_4)]^{-1} = 1.9$.

Even though it has been observed that agglomeration takes place in both processes, it is interesting to compare the observed growth rates to those calculated assuming a planar growth. Since these films had the anatase (101) as the most pronounced orientation the calculations are carried out using this plane as the growth plane. Also the amorphous films of the chloride process can be crudely modelled this way. The area per each TiO_2 unit projected on the anatase (101) plane ($A(TiO_2)_{(101)}$) is 10 $Å^2$, and the corresponding interlayer spacing $d_{(101)}$ is 3.5 Å. Assuming a close packing of the "precursor circles" (91% of the surface is covered by the circles) the theoretical growth rates per cycle can be calculated from the formula

$$v_g = 0.91[A(TiO_2)_{(101)}/A(\text{Ti–precursor})]d_{(101)} \quad (1)$$

where the ratio $A(TiO_2)/A(\text{Ti–precursor})$ gives the fraction of titanium sites occupied in the chemisorbed layer. This gives 0.99 Å/cycle for $TiCl_4$ and 0.52 Å/cycle for $Ti(OCH(CH_3)_2)_4$. The observed growth rates were lower than these, suggesting that the chemisorbed layer does not totally cover the surface of the growing film. This can be attributed to a localized adsorption which obstructs the close packing in the chemisorption layer. However, the effect of aggregation is likely to be important as well. As has been speculated,[10] the mechanism leading to aggregation may involve volatile species. By means of these species material can be lost from the chemisorption layer. Furthermore, also the number of active sites on the substrate surface may act as a limiting factor since in the chloride process different growth rates were observed on different substrate materials.[9] It should also be kept in mind that the calculations were based on molecule sizes which were only approximative. Despite of the crude approximations made and the difference between the calculated and observed growth rates it can be concluded that the achievable growth rate is largely dictated by the size of the precursor molecule.

Conclusions

ALE deposition of TiO_2 thin films with titanium isopropoxide and water as precursors was carried out. The temperature range for the self-controlled growth was limited below 350 °C by the thermal decomposition of $Ti(OCH(CH_3)_2)_4$. Despite the relatively low deposition temperature, the resulting films were of a high density and contained anatase phase in considerable quantities. Post annealing at 480 °C gave only a small increase in the film crystallinity with no observable thickness shrinkage.

A major obstacle to using $Ti(OCH(CH_3)_2)_4$ as an ALE precursor in place of $TiCl_4$ is the observed thickness nonuniformity. Additionally, the effective growth rate of the alkoxide process is only one-third of the chloride process. An obvious relationship between the maximum growth rates obtained and the sizes of the two titanium precursor molecules was pointed out.

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