



# In situ ellipsometry monitoring of TiO<sub>2</sub> atomic layer deposition from Tetrakis(dimethylamido)titanium(IV) and H<sub>2</sub>O precursors on Si and In<sub>0.53</sub>Ga<sub>0.47</sub>As substrates

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# *In situ* ellipsometry monitoring of TiO<sub>2</sub> Atomic Layer Deposition from TDMAT and H<sub>2</sub>O precursors on Si and In<sub>0.47</sub>Ga<sub>0.53</sub>As substrates

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## Abstract

TiO<sub>2</sub> Atomic Layer Deposition (ALD) is used in microelectronics due to its ability to produce conformal thin films whose thickness is controlled at the sub-nanometer scale. Tetrakis(dimethylamido)titanium(IV) (TDMAT) and water are frequently used precursors for TiO<sub>2</sub> ALD, although there are still some differences in growth behavior in the literature. In this parametrical study, the growth of TiO<sub>2</sub> was controlled *in situ* by Spectroscopic Ellipsometry (SE) in combination with *ex situ* thickness measurements by X-Ray Reflectometry (XRR). The injection and purge times were optimized to reach self-saturation on the surface. We put in evidence two regions of the Growth Per Cycle (GPC) as a function of substrate temperature: GPC decreases from 0.8 Å.cy<sup>-1</sup> to 0.5 Å.cy<sup>-1</sup> as the temperature rises from 50 °C to 200 °C, and then GPC increases from 0.6 Å.cy<sup>-1</sup> to 0.9 Å.cy<sup>-1</sup> as the temperature rises from 250 °C to 350 °C. There is

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\*Fully documented templates are available in the elsarticle package on CTAN.

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no evidence of an *ALD window*. The stoichiometry of the layer grown at 200 °C, determined by X-ray Photoelectron Spectroscopy (XPS), is TiO<sub>2</sub> (1 Ti atom per 2 O atoms). The 200 °C as-grown sample becomes crystalline (Anatase crystals) after annealing 3 hours in air at 400 °C, or at 600 °C. The initial growth stages of TiO<sub>2</sub> were studied by SE and Atomic Force Microscopy (AFM). Regarding TiO<sub>2</sub> ALD on (100)Si substrate (with a native SiO<sub>2</sub>), we observed a substrate enhanced growth which turned into steady-state ALD beyond 20-30 cycles. Additionally, TiO<sub>2</sub> ALD on (001)In<sub>0.53</sub>Ga<sub>0.47</sub>As substrate demonstrates substrate inhibited growth of type 2 (islands formation) which turned into TiO<sub>2</sub> steady-state ALD beyond 20-30 cycles. The results of TiO<sub>2</sub> ALD are compared with those of the existing literature.

*Keywords:* Atomic Layer Deposition; Spectroscopic Ellipsometry; TiO<sub>2</sub>; Oxides; TDMAT; Initial growth; Substrate Enhanced Growth; Substrate Inhibited Growth; InGaAs

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## 1. Introduction

Titanium dioxide (TiO<sub>2</sub>) or titania is a widely used material in microelectronics. The two polymorphs of titania - Anatase, and Rutile give TiO<sub>2</sub> its photocatalytic properties [1]. Titania is a transparent material in the near-  
5 infrared range. It has a high dielectric constant, a high refractive index. Thus, it finds a lot of applications in optics, catalysis, and electronics [2]. TiO<sub>2</sub> nano-  
materials, nanoparticles, thin films, and nanowires are synthesized by various chemical and physical methods [2] such as Sol-Gel Method [3], Chemical Vapor  
Deposition [4, 5], Magnetron-Sputtering [6], and others [7].

10 One of the best-used technics for TiO<sub>2</sub> thin film deposition and nanostructure coatings is Thermal Atomic Layer Deposition (ALD) which provides a low temperature (50-200 °C) TiO<sub>2</sub> growth with high conformality and precise subnanometer thickness control [8]. Thermal ALD [9] is a Chemical Vapor De-  
position (CVD) technique based on the self-limiting chemical reactions. The  
15 ALD process consists of ALD cycles. One cycle includes injections of precursors

(chemical compounds) that react with a temperature-controlled sample surface. In the case of  $\text{TiO}_2$  ALD [10], a metal-organic Ti precursor and oxygen precursor are injected in the reactor chamber one after another. In between the precursor injections, the reactor chamber is purged with inert gas to remove  
20 reaction products and the remaining parts of the precursor.

The  $\text{TiCl}_4$  (halide) precursor, one of commonly used Ti precursors, was used in early  $\text{TiO}_2$  growth experiments [11]. However, a disadvantage of halides is the corrosiveness of the reaction byproducts. For instance,  $\text{HCl}$  is a reaction product of  $\text{TiCl}_4$  with sample surface OH-group. Now, a lot of new Ti metalor-  
25 ganic precursors besides halides have been synthesized and used for ALD [10]: alkoxides, alkylamides, and heteroleptics. As oxidants [10], one can use  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{O}_2$ ,  $\text{O}_3$ ,  $\text{MeOH}$ ,  $\text{HCOOH}$ ,  $\text{CH}_3\text{COOH}$ , and some plasma sources (in case of Plasma Enhanced Atomic Layer Deposition – PEALD).

In this study, we consider the Atomic Layer Deposition using one of the most  
30 popular couples of precursors, *i.e.*  $\text{Ti}[(\text{CH}_3)_2\text{N}]_4$  or Tetrakis(dimethylamido)titanium(IV) (hereinafter TDMAT) and water. Despite the significant number of publication reporting on  $\text{TiO}_2$  ALD from TDMAT and water [12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 31, 33], there is no clear idea of all the possible chemical reactions on the surface during the growth process  
35 and also there is no unique behavior of growth curves (Growth Per Cycle) as a function of the growth temperature. Additionally, it was shown that the  $\text{TiO}_2$  initial growth stages depend on substrate chemistry, as in the case of  $\text{ZnO}$  ALD [34, 35, 36, 37],  $\text{TiO}_2$  exhibit different types of growth depending on the surface [15, 29].

40 In this article, we report on an extensive parametrical study of  $\text{TiO}_2$  ALD from TDMAT and water, by monitoring the growth *in situ* with spectroscopic ellipsometry. Our results are compared with those obtained by other groups to find an explanation of some differences in GPC temperature and initial growth stage behavior.

## 45 2. Experiment

TiO<sub>2</sub> Atomic Layer Deposition (ALD) was carried out with TDMAT as the Ti metalorganic precursor, water as an oxidant, and N<sub>2</sub> as a purging gas. TDMAT bubbler and water evaporator were kept at room temperature (25 °C) during the experiment. During the first ALD cycle pulse, TDMAT was injected  
50 into a closed reactor chamber carried by a 50 *sccm* flow of Ar gas that was flowing into the TDMAT bubbler. Then, during the second pulse, the reactor chamber was purged with a 1000 *sccm* flow of N<sub>2</sub> to remove excess TDMAT, Ar, and the products of the TDMAT reaction. During the third pulse, water steam was injected inside the reactor chamber (closed), using a deionized water  
55 evaporator without carrier gas. Finally, during the fourth pulse, the reactor chamber was purged out with a 1000 *sccm* flow of N<sub>2</sub>.

Silicon with a native SiO<sub>2</sub> layer on the top (from Sil'tronix) and In<sub>0.53</sub>Ga<sub>0.47</sub>As(270 nm)/InP (hereinafter InGaAs) substrates (from III-V lab, Palaiseau) were used for the experiment. SiO<sub>2</sub>/Si substrates were not chemically treated before the growth.  
60 InGaAs substrates were etched in 4M HCl solution for 3 *min*, rinsed in deionized water for 30s, and dried with N<sub>2</sub> to remove native surface oxides. Then, InGaAs substrates were immediately annealed in a vacuum inside the growth chamber at 200 °C for 30 *min* to remove atomic As on the surface [38, 34].

The growth was monitored *in situ* by spectroscopic ellipsometry. We used  
65 the 4 wavelengths (465 nm, 525 nm, 580 nm, and 635 nm) Film Sense FS-1<sup>TM</sup> Banded Wavelength Ellipsometer and FS-1 software for thickness calculation [39]. The final TiO<sub>2</sub> thickness was measured by X-Ray Reflectometry (XRR) using a SIEMENS D5000 (Bruker<sup>TM</sup>) reflectometer at the Cu K<sub>α</sub> wavelength and Bruker Leptos (version 6.03) software for the data analysis. The substrate  
70 and TiO<sub>2</sub> layer surface morphology was studied by an Atomic Force Microscopy (AFM) using a Dimension Icon Bruker<sup>TM</sup> microscope. The crystallographic transition was studied by Grazing Incidence X-Ray Diffraction (GIXRD) with a SmartLab (Rigaku<sup>TM</sup>) and Fourier-Transform Infrared Spectroscopy (FTIR) with VERTEX 70v FT-IR Spectrometer. During GIXRD measurements, the

75 incident angle between the x-ray beam and the sample surface was  $0.35^\circ$  (above  
the critical angle  $\alpha_c = 0.25^\circ$  for Cu  $K_\alpha$ ). The elemental composition of  $\text{TiO}_2$  was  
determined using X-ray Photoelectron Spectroscopy (XPS). XPS analyses were  
carried out in the K-alpha apparatus from Thermo Fisher Scientific. In an Ultra-  
High Vacuum (UHV) chamber ( $10^{-9}$  mbar), sample surfaces were irradiated  
80 with Al  $K_\alpha$  radiation ( $1486.6$  eV). The ejected electrons were collected by a  
hemispherical analyzer at  $30$  eV constant pass energy. The energy scale was  
calibrated with the C1s line from the contamination carbon at  $285.0$  eV. The  
measurements were carried out at a constant angle of  $90^\circ$  between the sample  
surface and the analyzer.

### 85 3. Results

#### 3.1. $\text{TiO}_2$ Atomic Layer Deposition parametric study

To build the ellipsometry model for the calculation of the  $\text{TiO}_2$  film thick-  
nesses, the refractive index  $n$  as a function of wavelength  $\lambda$  was determined by  
the Cauchy equation:

$$n(\lambda[nm]) = n_{633nm} + n_{slope}((1000/\lambda)^2 - (1000/633)^2), \quad (1)$$

90 where the constants  $n_{633nm} = 1.7$  and  $n_{slope} = 0.069$  were determined on the  
grown  $\text{TiO}_2$  sample with a known thickness, using the FS-1 software. The final  
 $\text{TiO}_2$  thickness was also checked by XRR measurements (see Fig. 1S and Table  
T1 in the Supplementary Information file). More information about ellipsometry  
measurements with the same equipment and software can be found in a previous  
95 study [35].

Here, we report on a parametrical study to optimize  $\text{TiO}_2$  ALD in our  
custom-built reactor [40, 34, 36, 35, 41, 37]. The main process parameters were  
varied, *i.e.* the duration of TDMAT injection ( $t_{TDMAT\ inj.}$ ), TDMAT purge  
( $t_{TDMAT\ purge}$ ), water injection ( $t_{H_2O\ inj.}$ ), and water purge ( $t_{H_2O\ purge}$ ), the  
100 water flow during water injection, as well as the substrate temperature. Also,  
we checked the influence of the substrate surface of growth on the early stage of

growth ((100)Si and (100)InGaAs/InP). The parametric study was performed on Si substrates.

First, we carried out TiO<sub>2</sub> ALD on Si for a series of samples by changing  
105  $t_{TDMAT\ inj.}$ : 2s, 5s, 7s, 10s, 20s, 30s, and 60s. The other injection/purge times  
 $t_{TDMAT\ purge}/t_{H_2O\ inj.}/t_{H_2O\ purge}$  were fixed to 30s/30s/45s, respectively; the  
water flow was 7.5 sccm; and the substrate temperature was 150 °C (this sub-  
strate temperature was often used for TiO<sub>2</sub> ALD using TDMAT and water  
[12, 14, 19, 21, 42, 25, 30, 32], it is lower than TDMAT decomposition tempera-  
110 ture [43], and high enough to avoid water condensation on the substrate surface  
[44, 42]).

Figure 1 shows the film thickness, measured *in situ* by ellipsometry, as a  
function of the number of cycles for different  $t_{TDMAT\ inj.}$  (injection time). The  
inset shows a zoom of one curve ( $t_{TDMAT\ inj.} = 60s$ ) corresponding to the cycle  
115 range 37 to 40. One can see that during TDMAT injection, the thickness starts  
to increase, then reaches a constant value. In contrast, during water pulse, the  
thickness decreases due to ligand exchange and OH-groups formation on the  
surface, then thickness reaches a constant value.

Comparing the thickness curves on Fig. 1, one can see that the steady  
120 growth rate increases for higher TDMAT injection times, till it reaches a maxi-  
mum value. Note that all the curves show a non-linear dependence as a function  
of cycle number, *i.e.* the first derivative of the mean thickness starts to decrease  
then becomes constant (steady growth). To determine the right TDMAT in-  
jection time value, we plotted the Growth Per Cycle (GPC) as a function of  
125 TDMAT injection time. First, we calculated GPC as a function of cycle num-  
ber as shown in the inset of Fig. 1: the GPC for cycle n is the variation in  
thickness observed between cycles n and (n-1), the thickness value is measured  
in the water purge region. Then, using this GPC function, we calculated the  
mean GPC value in the steady growth state region (for instance, for the curve  
130 corresponding to  $t_{TDMAT\ inj.} = 2s$ , this region is within the range of 30 to 50  
cycles). Figure 2(a) shows the mean GPC corresponding to the steady growth  
as a function of TDMAT injection time. The plot shows that increasing the

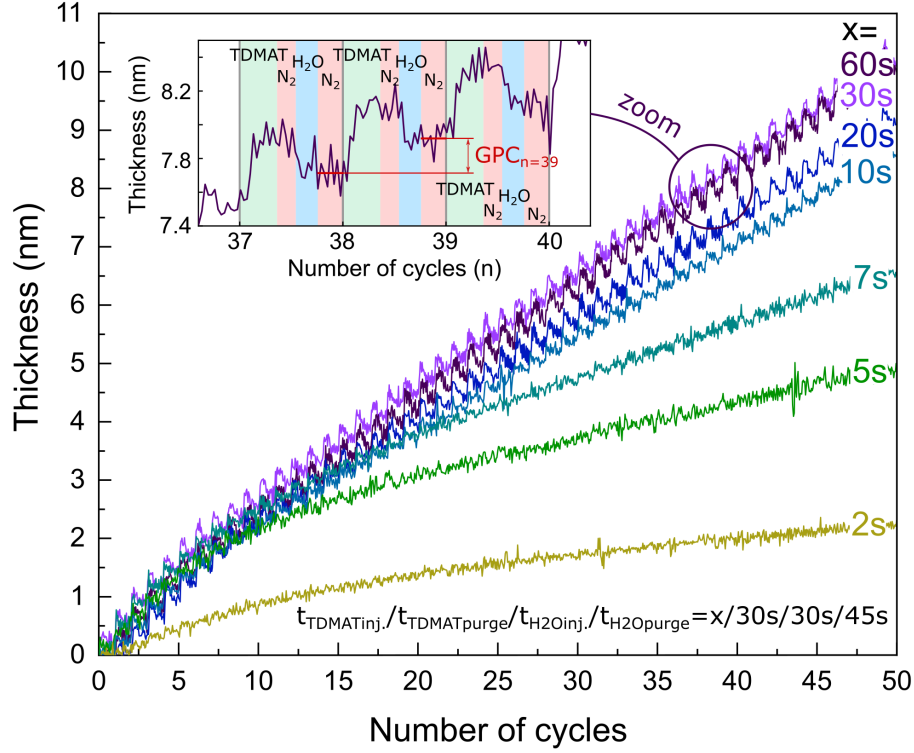


Figure 1:  $\text{TiO}_2$  thickness as a function of cycle number measured for different TDMAT injection time during growth (2s, 5s, 7s, 10s, 20s, 30s, and 60s). Inset: zoom of the 60s curve in the cycle range 37 to 40.

TDMAT injection time from 0 to 10s, the GPC linearly increases from 0 to  $1.6\text{\AA}.\text{cy}^{-1}$ . Then, the rate of GPC increase becomes smaller for injection times within the range of 10s to 30s. At about 30s injection time, the GPC reaches a plateau at a constant value close to  $1.9\text{\AA}.\text{cy}^{-1}$ . Since TDMAT injection time has to be low enough to save experimental time and prevent the waste of precursor, but high enough to reach self-limiting surface saturation (GPC plateau), it was fixed to 10s (green open circle on Fig.2(a)).

After optimizing the TDMAT injection time, we optimized the TDMAT purge time ( $t_{\text{TDMAT purge}}$ ). The pulse times  $t_{\text{TDMAT inj.}}/t_{\text{TDMAT purge}}/t_{\text{H}_2\text{O inj.}}/t_{\text{H}_2\text{O purge}}$  were fixed to  $10\text{s}/x/30\text{s}/45\text{s}$ , respectively, where  $x = t_{\text{TDMAT purge}}$  was fixed to 5s, 30s, 60s, and 180s. Fig.2(b) shows GPC as a function of TDMAT purge



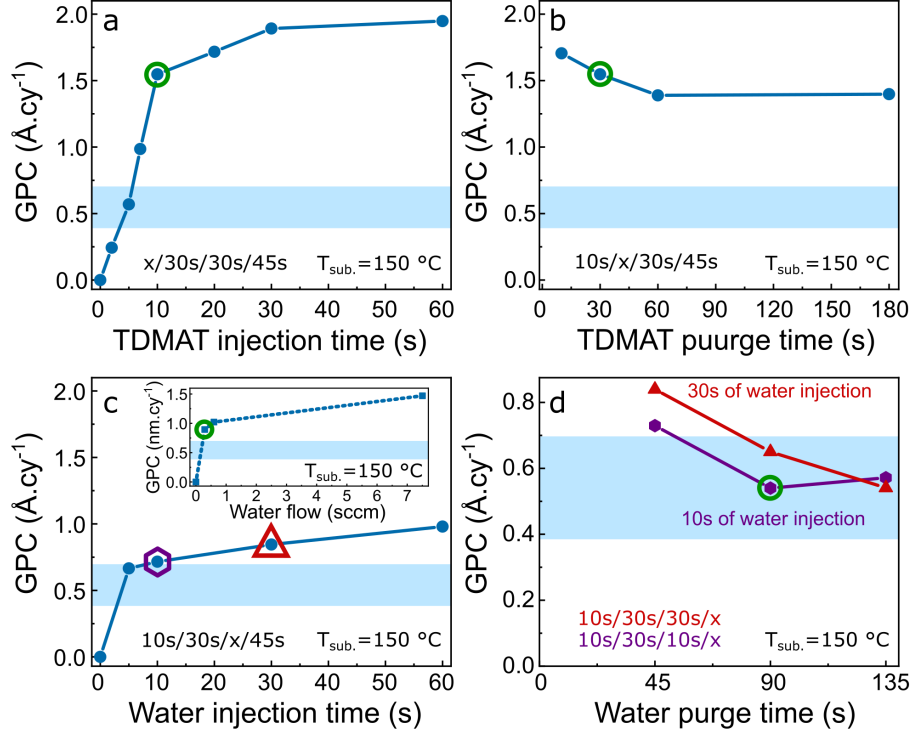


Figure 2: Growth Per Cycle (GPC) as a function of TDMAT injection time (a), TDMAT purge time (b), water injection time (c), water flow (c, inset), and water purge time (d). The green open circles on the figure show our optimized growth parameters. Violet solid hexagons and red solid triangles on panel (d) show the GPC behavior for 10s and 30s water injection times, respectively. The light blue area in the background indicates the range of expected  $\text{TiO}_2$  GPC values as found in the literature [12, 14, 19, 21, 42, 25, 30, 32].

time. Increasing TDMAT purge time from 5s to 180s, the GPC decreases from  
145  $1.6\text{\AA}\cdot\text{cy}^{-1}$  to  $1.4\text{\AA}\cdot\text{cy}^{-1}$ . We decided to fix the TDMAT purge time to 30s (green  
open circle on Fig.2(b)).

Although TDMAT injection and purge times were optimized, the total GPC  
for this substrate temperature ( $150\text{ }^{\circ}\text{C}$ ) is higher than GPC found in the litera-  
ture [12, 14, 19, 21, 42, 25, 30, 32] (light blue region on figure.2(a)-2(d)). Thus,  
150 we checked the influence of water injection and purge times on the process.  
Since the reactor chamber was closed during water pulse, an increase of water  
flow and/or water injection time results in an increase of water amount inside

the reactor chamber. Figure 2(c) shows steady GPC values as a function of water injection time,  $t_{H_2O\ inj.}$  with  $t_{TDMAT\ inj.}/t_{TDMAT\ purge}/t_{H_2O\ purge}$  fixed to 10s/30s/45s; and water flow fixed to 0.3 *sccm*. The inset of Fig. 2(c) shows the GPC as a function of water flow values. Both GPC curves increase for higher water injection time or flow, then reach a constant value. The optimized water flow was fixed to 0.3 *sccm* (green open circle), and the water injection time to 10s (violet open hexagon) or 30s (red open triangle).

Figure 2(d) shows two GPC curves obtained upon water purge time, for 10s of water injection (violet solid hexagones) and 30s of water injection (red solid triangles),  $t_{TDMAT\ inj.}/t_{TDMAT\ purge}$  were fixed to 10s/30s. Both curves reach the same value equal to  $0.55\text{\AA}.\text{cy}^{-1}$  for 135s water purge time, and for both curves, the GPC decreases when the water purge time increases. However, in comparison to 30s of water injection, lower water purge times are needed to reach the GPC plateau for 10s of water injection.

Based on this, we chose the following process parameters:  $t_{TDMAT\ inj.}/t_{TDMAT\ purge}/t_{H_2O\ inj.}/t_{H_2O\ purge}$  equal to 10s/30s/10s/90s, respectively and the water flow equal to 0.3 *sccm*, to determine the GPC versus the substrate temperature. Figure 3 shows the experimental GPC values as a function of substrate temperature determined in this study (blue solid circles), as well as values from the literature [12, 14, 19, 21, 42, 25, 30, 32] obtained for ALD  $\text{TiO}_2$  layers grown from TDMAT and water.

It clearly appears that the GPC behavior as a function of the growth temperature can be divided into two regions: the GPC decreases from  $0.8\text{\AA}.\text{cy}^{-1}$  to  $0.5\text{\AA}.\text{cy}^{-1}$  as the temperature rises from  $50\text{ }^\circ\text{C}$  to  $200\text{ }^\circ\text{C}$ , then it increases from  $0.6\text{\AA}.\text{cy}^{-1}$  to  $0.9\text{\AA}.\text{cy}^{-1}$  as the temperature rises from  $250\text{ }^\circ\text{C}$  to  $350\text{ }^\circ\text{C}$ . The origin of this behavior is discussed hereafter in the Discussion section (section 4).

### 3.2. Stoichiometry of $\text{TiO}_2$ amorphous layers and $\text{TiO}_2$ crystallization after annealing

To check the stoichiometry of the ALD  $\text{TiO}_2$  layers and chemical states of Ti and O atoms, we performed X-ray Photoelectron Spectroscopy (XPS) measure-

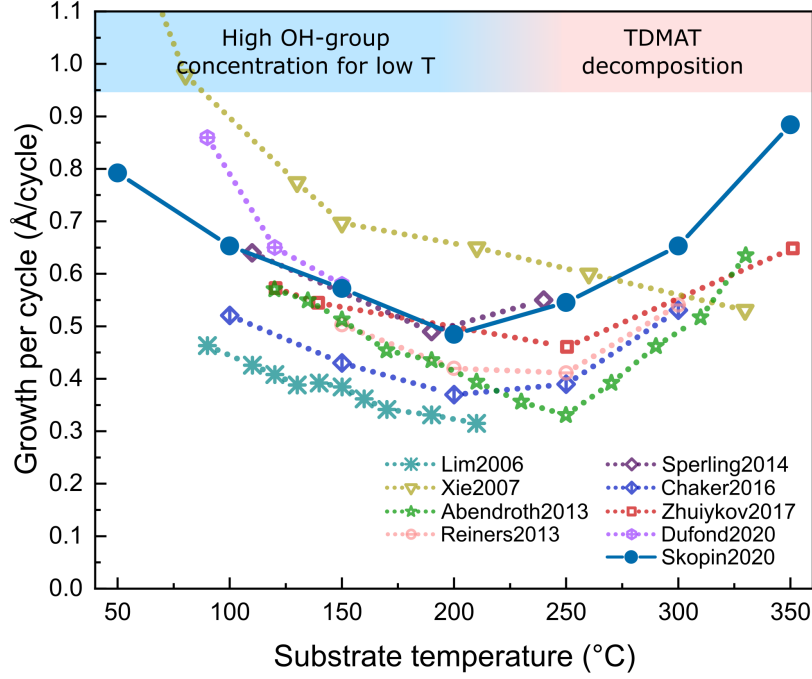


Figure 3: Experimental Growths Per Cycle (GPCs) as function of substrate temperature: present study (blue solid circles, solid line), and from the literature [12, 14, 19, 21, 42, 25, 30, 32](different types of open symbols, dashed lines).

ments. Here, we give the results for a sample obtained with the following growth conditions: 200 °C, 275 cycles, deposition times equal to 10s/30s/10s/45s (see Fig.2(d)). The water flow during deposition was set to 0.3 *sccm*. The XPS signal was measured from the as-grown TiO<sub>2</sub> subsurface, and then the measurement was repeated after 3 *min* of a surface etching by Ar plasma (approximately 3-4 *nm* thick TiO<sub>2</sub> layer was etched). Figure 4(a) shows Ti2p XPS lines measured before Ar etching, other XPS lines before and after etching are presented in the Supplementary Information (figure S2). The Ti2p spectra consists of Ti2p<sub>3/2</sub> and Ti2p<sub>1/2</sub> peaks (doublet). The peak positions correspond to the ones of stoichiometric TiO<sub>2</sub> [32, 45, 46]. Other elements were also found in the layer: O, N, and C. Integrating the area for every element and using the relative sensitivity factors (RSF) method, we calculated the atomic percent of every element in the

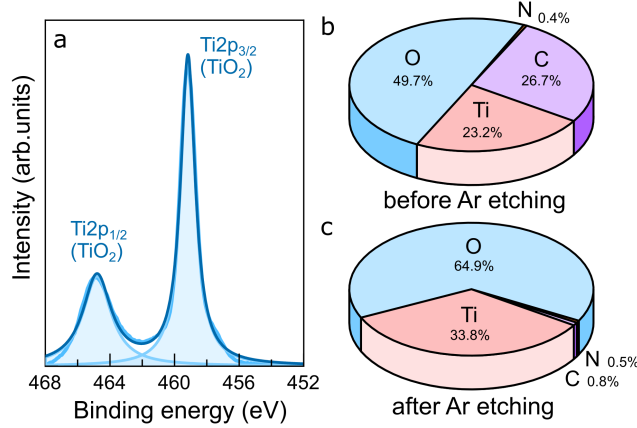


Figure 4: X-ray Photoelectron Spectroscopy (XPS) of Ti 2p lines (doublet): intensity as a function of binding energy measured before Ar plasma etching (a); element concentrations in  $\text{TiO}_2$  layer in atomic percent measured before (b) and after (c) Ar plasma etching.

195 film. Figure 4(b) shows the atomic percent of the film surface and subsurface before plasma etching, *i.e.* 23.2%, 49.7%, 0.4%, and 27.7% of Ti, O, N, and C; respectively. After Ar plasma etching (figure 4(c)), the C content almost drops down to zero, and the relative concentration of Ti, O, and N stays the same, *i.e.* 33.8%, 64.9%, 0.5%, 0.8% of Ti, O, N, and C, respectively. Thus, before  
200 and after plasma etching, the  $\text{TiO}_2$  stoichiometry is approximately one Ti atom for every two O atoms.

Grazing Incidence X-Ray Diffraction (GIXRD) and Fourier-Transform Infrared Spectroscopy (FTIR) measurements showed that the sample grew at 200 °C is non-crystalline. For improving the crystallinity of the as-deposited  
205  $\text{TiO}_2$  layer we annealed a set of samples deposited at 200 °C on Si substrate (same growth conditions as mentioned in the first paragraph of this section) in the air for 3h at 400 °C and 600 °C.

Figure 5(a) shows GIXRD diagrams measured for the as-deposited and annealed  $\text{TiO}_2/\text{Si}$  samples. After annealing one can observe the Bragg peaks of  $\text{TiO}_2$  Anatase structure (ICSD 9852, PDF 01-071-1166), regardless of the  
210 annealing temperature. On all diagrams one can see a bump located around 50-60°, we suppose that it is caused by the diffuse scattering from the Si substrate.

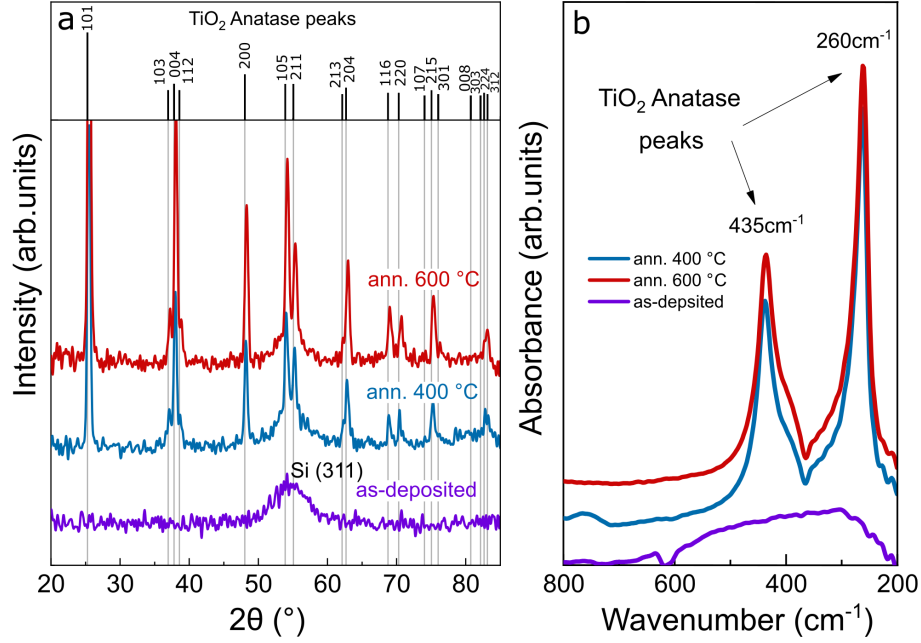


Figure 5: Grazing Incidence X-Ray Diffraction (GIXRD) (a) and Fourier-transform infrared spectroscopy (FTIR) (b) curves measured for the as-deposited sample (deposition temperature was 200  $^\circ\text{C}$ ) and for samples annealed at 400  $^\circ\text{C}$  and 600  $^\circ\text{C}$ .

FTIR measurements (figure 5(b)) confirm the same result with the presence of the two characteristic peaks of TiO<sub>2</sub> Anatase [47] at 435  $\text{cm}^{-1}$  and 260  $\text{cm}^{-1}$ .

### 3.3. TiO<sub>2</sub> initial growth on Si and In<sub>0.53</sub>Ga<sub>0.47</sub>As

In this section, we report on a study of the early growth of ALD TiO<sub>2</sub> on (100)InGaAs and (100)Si substrates. The latter being covered with native silicon oxide. The deposition temperature was 150  $^\circ\text{C}$  and the  $t_{\text{TDMAT inj.}}/t_{\text{TDMAT purge}}/t_{\text{H}_2\text{O inj.}}/t_{\text{H}_2\text{O purge}}$  were 10s/30s/30s/45s, respectively, the water flow was 0.3 *sccm*. We grew a series of samples with 2, 5, 10, and 15 cycles. The InGaAs substrate surface presents atomically flat terraces, therefore the surface morphology change could be easily detected by Atomic Force Microscopy (AFM). Figure S3 in Supplementary Information shows AFM images for ALD TiO<sub>2</sub> on InGaAs and Si.

Figures 6(a) and 6(b) show the *in situ* GPC versus cycle number for ALD TiO<sub>2</sub> grown on InGaAs and Si, respectively. The insets of Figs. 6(a) TiO<sub>2</sub>/InGaAs

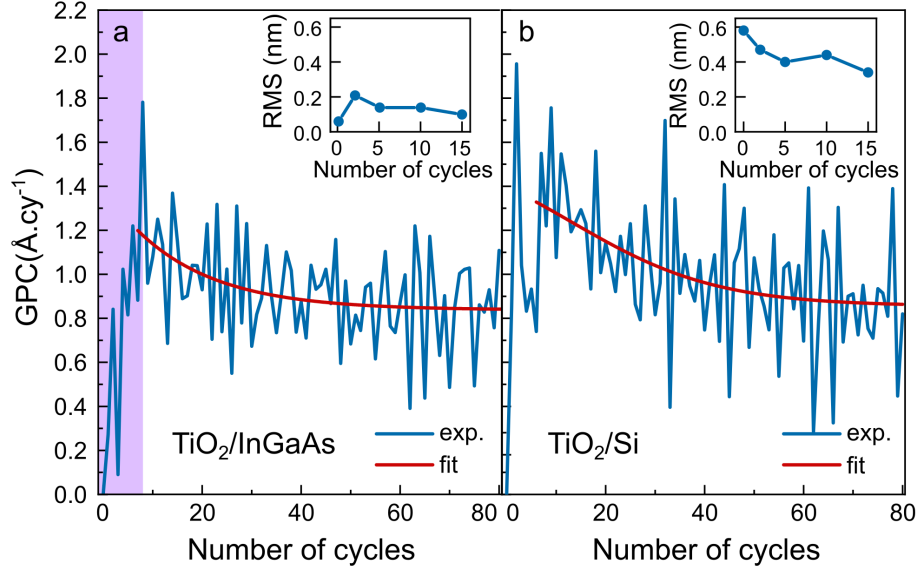


Figure 6: GPC versus cycle number measured during TiO<sub>2</sub> ALD on InGaAs (a) and Si (b). The light violet area on the left panel (a), highlight the region where the GPC increases. The figure insets show the surface roughness (root mean squared roughness).

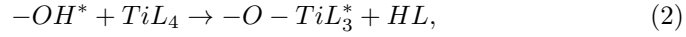
and 6(b) TiO<sub>2</sub>/Si show TiO<sub>2</sub> surface Root Mean Squared (RMS) roughness, calculated using a series of AFM images (image size was  $(1 \times 1) \mu m^2$ ), as a function of the number of cycles.

Each GPC curve for TiO<sub>2</sub>/InGaAs and TiO<sub>2</sub>/Si has transient growth region prior to linear growth (constant GPC). One can observe that the GPC of TiO<sub>2</sub> ALD on InGaAs can be divided into three regions, at the early stage it increases up to a maximum (light violet area), then slightly decreases before reaching a constant value. In comparison, in the case of TiO<sub>2</sub>/Si, the growth region corresponding to the increase of GPC is absent. Beyond cycle 2, both GPC curves demonstrate the same behavior. The red lines on the GPC curves represent the Sigmoid function fits, plotted for better data visualization.

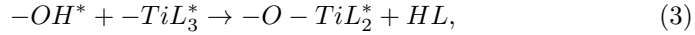
At the same time, beyond 2 ALD cycles the RMS roughness of ALD TiO<sub>2</sub>/InGaAs increases whereas it decreases for ALD TiO<sub>2</sub>/Si. Then, increasing the number of cycles, TiO<sub>2</sub> roughness starts to decrease both for TiO<sub>2</sub>/InGaAs and TiO<sub>2</sub>/Si.

## 240 4. Discussion

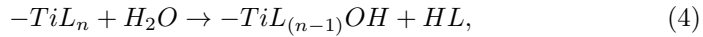
In an attempt to explain our results about the growth of  $\text{TiO}_2$  by ALD, we need to describe the possible chemical reactions on the growth surface. In the present study, one cycle of thermal  $\text{TiO}_2$  ALD from TDMAT and water consists of four pulses: TDMAT injection, TDMAT purge ( $\text{N}_2$ ), water injection, and  
 245 water purge ( $\text{N}_2$ ). As shown by experiments, Density Functional Theory (DFT) and Monte-Carlo (MC) simulations [14, 42, 12, 19, 30], TDMAT interaction with OH-terminated surface can be formally described by the following chemical reaction:



where  $-\text{OH}^*$  is a hydroxyl group on the  $\text{TiO}_2$  surface (\* denotes the surface species),  $\text{TiL}_4$  is a TDMAT molecule, L (or  $\text{N}(\text{CH}_3)_2$ ) a TDMAT ligand, and  
 250 HL ( $\text{H}(\text{N}(\text{CH}_3)_2)$ ) the dimethylamine (DMA). Then,  $\text{TiL}_3$ , chemisorbed on the surface, can react with another surface OH-group and lose one ligand L to form DMA:



After reaction with TDMAT,  $\text{TiO}_2$  surface becomes L-terminated, and the  
 255 reaction products are eliminated. During water injection,  $\text{H}_2\text{O}$  reacts with L-terminated  $\text{TiO}_2$  surface:



Finally,  $\text{TiO}_2$  surface becomes OH-terminated, and the reaction products of the are purged. Then, a new ALD cycle can start.

### 4.1. Growth per cycle as a function of substrate temperature

260 Experiments and calculations show that the GPC depends on the chemical reactions between the selected precursors and the sample surface, which strongly depend on the surface temperature [8]. Dufond *et al.* [32], using Density Functional Theory (DFT) and Monte Carlo (MC) calculations, showed that the volume of the TDMAT molecule is rather large ( $220.4 \text{ \AA}^3$ ) and that the

265 GPC falls in the range of [0.18-0.26] monolayer/cycle, depending on the substrate temperature. The GPC is lower than the Anatase lattice parameters  $a = 3.78520\text{\AA}$ ,  $c = 9.51390\text{\AA}$  (ICSD 9852, PDF 01-071-1166), this can be explained by the TDMAT steric hindrance.

As shown in figure 3, the substrate temperature is a factor that strongly  
270 influences the GPC. To explain the GPC behavior and connect it with chemical reactions (2), (3) and (4) that happen on the surface, growth is considered in two temperature ranges (below or above than  $200\text{ }^{\circ}\text{C}$ ).

First, let us consider reaction (2) in the low-temperature range ( $50\text{-}200\text{ }^{\circ}\text{C}$ ). Xie *et al.* [14] showed that TDMAT molecule can be easily chemisorbed on  $\text{TiO}_2$   
275 surface covered with OH-groups. This reaction can occur at all temperatures (from room temperature upwards).

Reaction 4 determines the number of OH-groups on the growth surface and has an impact on GPC. Walle *et al.* [44], using synchrotron radiation core level photoelectron spectroscopy (XPS), showed that concentration of OH-groups and  
280 water molecules on the  $\text{TiO}_2$  surface decreases while increasing the surface temperature. Consequently, one can expect higher GPC at lower substrate temperatures due to an increase in the number of active surface sites (OH-groups, water molecules, protons) to react with TDMAT. Indeed, using *in situ* reflection-absorption infrared spectroscopy (RAIRS) during  $\text{TiO}_2$  ALD from TDMAT and  
285 water precursors, Sperling *et al.* [42] showed that water molecules are present on the growth surface at  $110\text{ }^{\circ}\text{C}$  and  $190\text{ }^{\circ}\text{C}$ . Instead, the authors showed that at  $240\text{ }^{\circ}\text{C}$ , water molecules on the surface are not consumed by TDMAT, indicating that water has desorbed from the surface during the TDMAT pulse. In general, several studies [12, 14, 19, 21, 42, 25, 30, 32], including ours, demonstrate that the GPC decreases as the substrate temperature increases in the  
290 low-temperature range.

Now, for higher substrate temperatures ( $T_{\text{sub.}} > 200\text{ }^{\circ}\text{C}$ ), the density of the OH-groups on  $\text{TiO}_2$  surface is expected to decrease [44] resulting in a decrease in total CPC which can be offset by an increase due to the decomposition of the  
295 TDMAT precursor molecules. Driessen *et al.* [43] used infrared spectroscopy *in*



*situ* to study the TDMAT decomposition on the growth surface. They showed that for substrate temperatures higher than 200 °C, TDMAT decomposes and forms  $\text{TiN}_x\text{C}_y$  compounds on the surface. They showed that time is an important parameter in the TDMAT decomposition process. Given their experimental condition, it was necessary to wait several minutes to decompose all the TDMAT precursor amounts and increasing the substrate temperature the decomposition becomes faster. Sperling *et al.* [42] used XPS to check whether a higher carbon concentration is detected in the material grown at higher temperatures (240 °C) during the ALD process. They found that the C concentration during the real  
300 ALD process decreases as a function of substrate temperature (1.4, 0.7, 0.7 at.% at 110, 190, 240 °C, respectively).

Besides, Xie *et al.* [14], using DFT calculations, suggested that during ALD, the desorption of the intermediate product of the reaction, *i.e.*  $\text{TiL}_3\text{-OH}$ , is possible, although the energy barrier is quite high (1.39 eV). The authors  
310 experimentally demonstrated that this effect can contribute to the decreasing of the GPC at high temperatures (greater than 200 °C). Thus, both the  $\text{TiL}_3\text{-OH}$  desorption from the surface and the TDMAT decomposition on the surface influence the GPC values in the high-temperature range of growth. Figure 3 shows that the experimental GPC increases in the high-temperature range of growth as reported in almost all studies of  $\text{TiO}_2$  ALD from TDMAT and water.  
315 Since the chemical reactions during TDMAT pulse are no longer self-limited at high temperatures, the GPC values depend on the amount of injected TDMAT. As a consequence, GPC values in the reported literature[19, 21, 42, 25, 30, 32] are not consistent.

#### 320 4.2. The initial $\text{TiO}_2$ growth

The incipient  $\text{TiO}_2$  ALD from TDMAT and water is different for (100)InGaAs or (100)Si (covered with native oxide) surfaces, but in both cases, a transient regime of growth precedes the steady-state one. As shown in figure 6(a), the early stage of  $\text{TiO}_2$  ALD on (100)InGaAs is typical of a substrate-inhibited  
325 growth of type 2 [48] (GPC increases, reaches the maximum, then starts to

decrease before reaching a constant value corresponding to the steady-state of growth). Instead,  $\text{TiO}_2$  ALD on Si (Fig. 6(b)) is typical of a substrate-enhanced growth [48] (GPC is maximum at the first cycle, then starts to decrease to reach a constant value).

330 Similarly to the previous case, Dendooven *et al.* [15], using *in situ* Ti X-Ray Fluorescence (XRF) monitoring during  $\text{TiO}_2$  ALD from TDMAT and water, demonstrated a substrate-enhanced growth of  $\text{TiO}_2$  on  $\text{Al}_2\text{O}_3$  surface. They hypothesized that  $\text{Al}_2\text{O}_3$  surface had a higher surface density of OH-groups than the  $\text{TiO}_2$  surface. They also showed that  $\text{TiO}_2$  GPC grown on HF-etched  
335 Si surface is low at the beginning of growth, then it rises and reveals a substrate-inhibited growth of type 2 [48]. The authors assigned the low GPC value during the first cycles to the lower OH-group concentration on the HF-treated Si surface than on  $\text{TiO}_2$  surface.

Interestingly, Ye *et al.* [29], using *in situ* infrared spectroscopy during  $\text{TiO}_2$   
340 ALD on GaAs, demonstrated that chemical adsorption of TDMAT is higher to chemical oxide on GaAs surface (their substrates were treated for 30 *min* in an aqueous  $\text{H}_2\text{O}_2$  solution to grow a chemical oxide layer, followed by a deionized water rinse and  $\text{N}_2$  blow-dry) than to as-grown  $\text{TiO}_2$  surface, possibly leading to substrate enhanced growth.

345 In our previous ALD study [34, 35, 36, 37], we showed that the early stage of growth of ZnO ALD on (100)InGaAs surface from Diethylzinc and water, is a substrate-inhibited growth of type 2, as in the case of  $\text{TiO}_2$  ALD on (100)InGaAs. As for  $\text{TiO}_2$  ALD on InGaAs, the most likely explanation for the GPC behavior in the early stage of growth, is the surface roughening (see inset of Fig.  
350 6(b)). After the first cycle, the surface area available for the reaction increases due to the formation of nuclei or islands and leads to the increasing of the GPC [34]. Then, the surface becomes smooth (the surface area decreases), and GPC decreases to reach a constant value.

With respect to the case ZnO ALD on (100)InGaAs, the origin of higher  
355  $\text{TiO}_2$  GPC during the first cycles on Si (covered with a native Silicon oxide) is likely due to a higher density of OH-groups (or water molecules) on the native

Si oxide surface than on the grown material surface.

#### 4.3. Crystallization of amorphous $\text{TiO}_2$ layers

Most studies on  $\text{TiO}_2$  thermal ALD, using TDMAT and water as precursor  
360 and oxidant, show that  $\text{TiO}_2$  thin films are amorphous (according to XRD) after  
deposition at temperatures less than  $250^\circ\text{C}$  on (100)Si covered with native  
 $\text{SiO}_2$  [19, 31, 12, 14], (100)Si without native oxide [32],  $\text{SiO}_2(430\text{ nm})/\text{Si}$  [21],  
 $\text{RuO}_2/\text{Ru}$  electrodes grown on  $\text{SiO}_2/\text{Si}$  [25], and SiC fiber bundles [24].

Chaker *et al.* [25] showed that as-deposited 18 nm-thick  $\text{TiO}_2$  layers, grown  
365 at  $250^\circ\text{C}$  from TDMAT and water, is composed of  $\text{TiO}_2$  Anatase with a small  
amount of  $\text{TiO}_2$  Rutile crystalline phases. Abendroth *et al.* [19] showed that as-  
deposited 47 nm-thick  $\text{TiO}_2$  layer, grown at  $320^\circ\text{C}$  from TDMAT and water,  
both  $\text{TiO}_2$  Anatase and Rutile phases are detected. The authors found that  
10 nm-thick  $\text{TiO}_2$  layer grown at  $250^\circ\text{C}$ , is amorphous, whereas, for higher  
370 thicknesses, the nucleation of crystalline phases is initiated inside the layer.  
For deposition temperatures higher than  $250^\circ\text{C}$ , nucleation of the crystalline  
layer can start directly on the (100)Si substrate (covered with a native  $\text{SiO}_2$   
layer). Reiners *et al.* [21] found different crystalline phases of  $\text{TiO}_2$  deposited  
at different substrate temperatures (using TDMAT and water): up to  $200^\circ\text{C}$  -  
375 no crystalline phases; at  $250^\circ\text{C}$  - the brookite and Anatase phases; at  $300^\circ\text{C}$   
- the Brookite, Anatase, and Rutile phases.

Summarizing the experimental findings from the literature, one can say that,  
for substrate temperature equal to or greater than  $250^\circ\text{C}$ , the  $\text{TiO}_2$  crystal-  
lization starts during the ALD process [32].

380 In the present study, we have shown that as-deposited, about 14 nm-thick  
 $\text{TiO}_2$  layer, grown at  $200^\circ\text{C}$  on (100)Si, is amorphous. And it becomes crys-  
talline after 3 hours of annealing in air. Regardless of the temperature,  $400^\circ\text{C}$   
or  $600^\circ\text{C}$ , the crystalline phase is Anatase.

Several annealing experiments reported in previous studies are in agreement  
385 with our results. Lim *et al.* [12] showed that ALD  $\text{TiO}_2$  layer deposited at  
 $150^\circ\text{C}$  (from TDMAT and water) is amorphous. After annealing 3 hours in the

air it becomes crystalline and shows the presence of Anatase phase at annealing temperatures in the range [300-400 °C], both Anatase and Rutile phases in the range [500-700 °C], and only Rutile phase at 800 °C. Cao *et al.* [24] showed that 70 nm-thick ALD TiO<sub>2</sub> (from TDMAT and water) layer grown at 150 °C is amorphous, it becomes crystalline after a thermal treatment. Annealing for one hour in the air at 600 °C leads to Anatase; 1000 °C to Anatase and Rutile; then 1400 °C to Rutile. Xie *et al.* [14] showed that ALD TiO<sub>2</sub> deposited layers at 150 °C (from TDMAT and water) are amorphous, they crystallize to Anatase after annealing in the temperature range [400-600 °C].

## 5. Conclusion

Using *in situ* Spectroscopic Ellipsometry (SE) and together with post-growth X-Ray Reflectometry (XRR), we monitored TiO<sub>2</sub> ALD on Si and InGaAs substrates. We found that the TiO<sub>2</sub> ALD from TDMAT and water precursors can be split into two temperature regions: a low-temperature range (50-200 °C) in which GPC decreases from 0.8 Å.cy<sup>-1</sup> to 0.5 Å.cy<sup>-1</sup> and high-temperature range (250-350 °C) in which GPC increases from 0.6 Å.cy<sup>-1</sup> to 0.9 Å.cy<sup>-1</sup>. In the low-temperature range, GPC is mainly influenced by the concentration of OH-groups (or water molecules) on the TiO<sub>2</sub> surface, which decreases as the substrate temperature increases. In the high-temperature range, GPC is influenced by the decomposition of TDMAT precursor on the TiO<sub>2</sub> surface, which leads to more active surface sites for reaction with water molecules. We found that water purge takes time in the low-temperature range, this may explain the different final GPC values reported in the literature. In the high-temperature region, the GPC difference reported in the literature can be explained by the different TDMAT pulse time leading to different amounts of TDMAT molecules for the chemical reactions, since the decomposition of TDMAT strongly depends on the time of reaction at this temperature range. We demonstrated that the 14 nm TiO<sub>2</sub> layer grown at 200 °C is amorphous and can be crystallized to Anatase after annealing. We found that the initial stages of TiO<sub>2</sub> ALD depend

on the substrate surface, *i.e.* a substrate-enhanced growth on SiO<sub>2</sub>/Si surface and substrate-inhibited growth on InGaAs surface.

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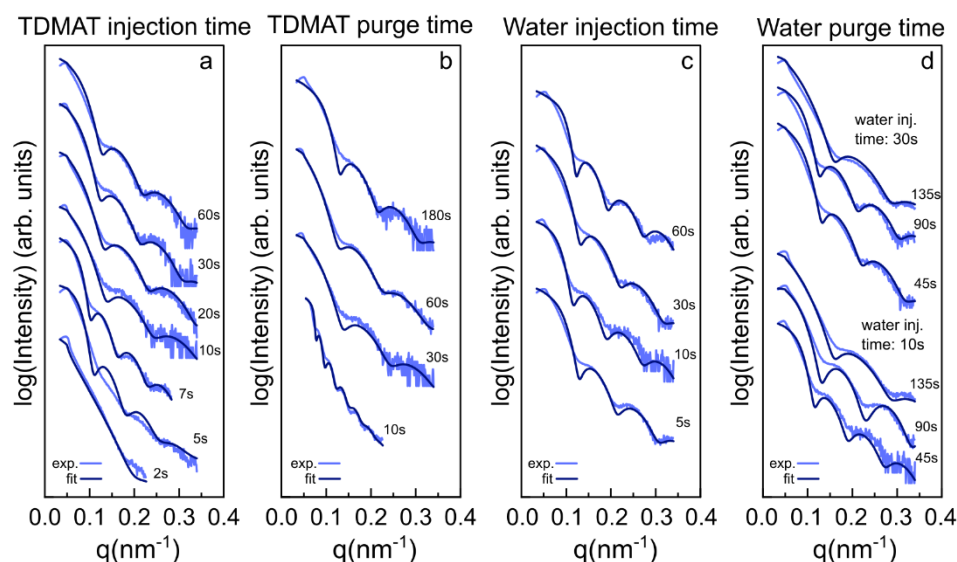
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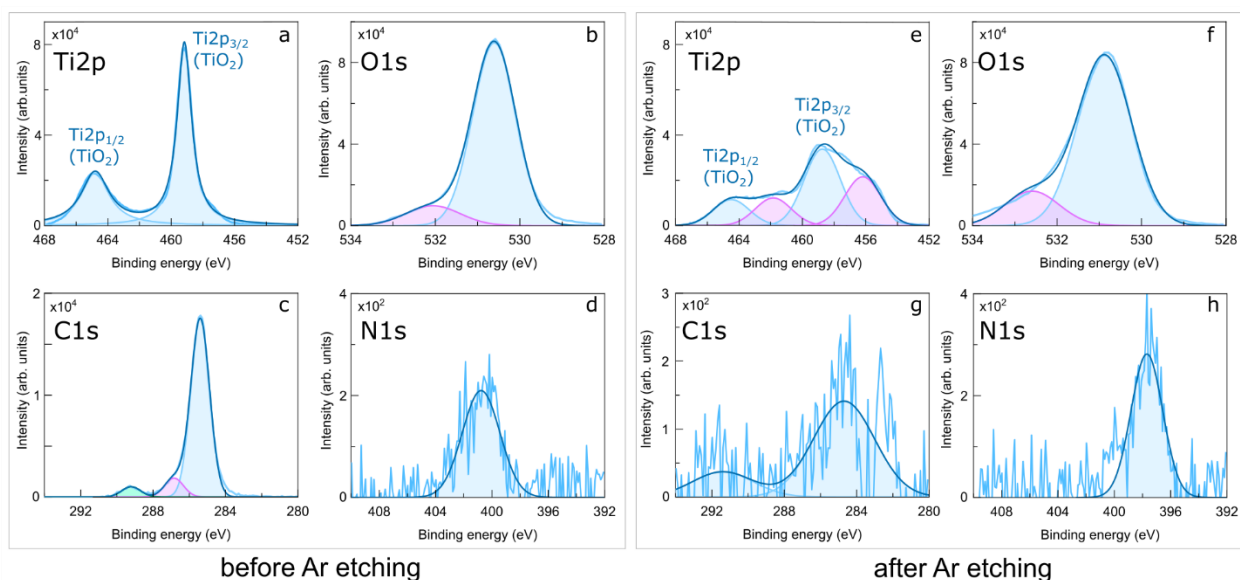
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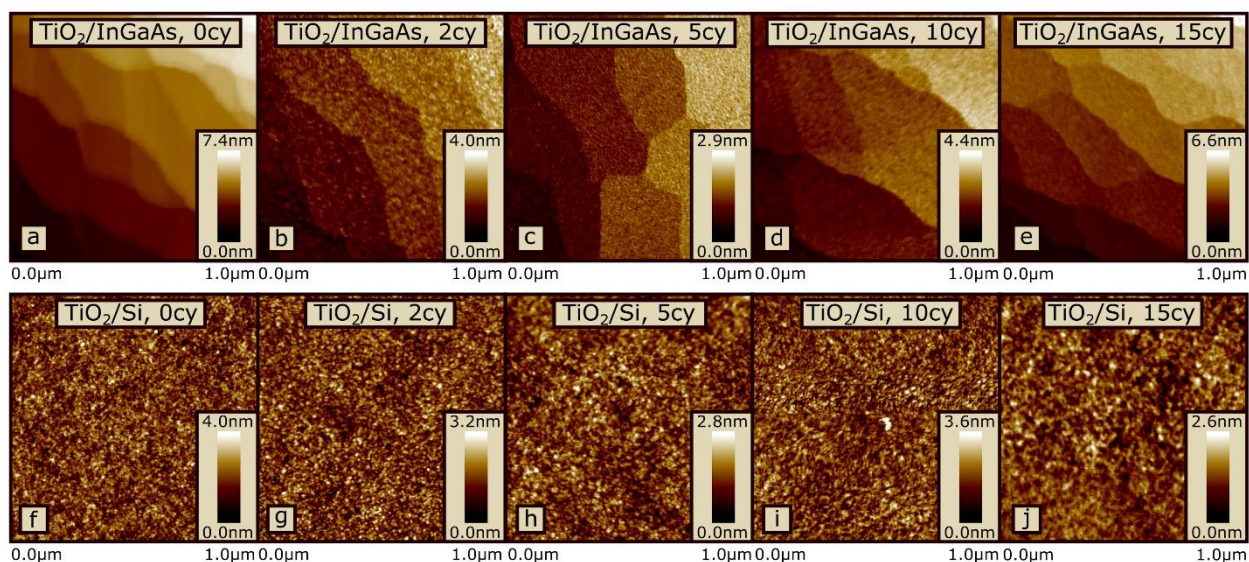
**Figure S1.** X-Ray Reflectivity (XRR) curves, measured after the growth of TiO<sub>2</sub>/Si samples. The different purge/pulse parameters were varied: (a) TDMAT pulse time was 2, 5, 7, 10, 20, 30, 60s; (b) TDMAT purge time was 10, 30, 60, 180s; (c) Water pulse time was 5, 10, 30, 60s; and (d) Water purge time was 45, 90, 130s for fixed water pulse time at 10s and 30s.

**Table T1.** The thickness of TiO<sub>2</sub> layers obtained after experimental x-ray reflectivity curves fit.

Parameter		Time (s)	Number of cycles	TiO <sub>2</sub> thickness (nm)
TDMAT injection time		60	50	9.7±0.5
		30	50	10.3±0.3
		20	50	9.1±0.6
		10	50	8.6±1.1
		7	120	13.7±0.6
		5	150	12.0±1.6
		2	185	5.4±1.1
TDMAT purge time		180	60	10.1±0.4
		60	60	9.2±1.2
		30	50	8.6±1.1
		10	200	29.9±5.5
Water injection time		60	100	11.6±0.4
		30	100	9.8±0.3
		10	130	11.5±0.8
		5	140	10.1±0.7
Water purge time	10s of water injection	135	125	7.2±0.2
		90	150	9.2±0.1
		45	130	11.5±0.8
	30s of water injection	135	130	8.0±0.3
		90	140	10.2±0.3
		45	100	9.8±0.3



**Figure S2.** X-ray photoelectron spectroscopy (XPS) lines of a 14nm thick amorphous  $\text{TiO}_2$  layer measured before (a-d) and after (e-h) Ar plasma etching: (a,e)  $\text{Ti}2p$ , (b,f)  $\text{O}1s$ , (c,g)  $\text{C}1s$ , (d,h)  $\text{N}1s$ .



**Figure S3.**  $(1 \times 1) \mu\text{m}^2$  AFM images measured for (a-e)  $\text{TiO}_2/\text{InGaAs}$  and (f-j)  $\text{TiO}_2/\text{Si}$  series of samples with a different number of ALD cycles: (a,f) 0cy or substrate, (b,g) 2cy, (c,h) 5cy, (d,i) 10cy, and (e,j) 15cy.