SUPPORTING INFORMATION

Impact of ions on film conformality and crystallinity during plasma-assisted atomic layer deposition of TiO₂

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Abstract of corresponding article: This work demonstrates that ions have a strong impact on the growth per cycle (GPC) and material properties during plasma-assisted atomic layer deposition (ALD) of TiO₂ (titanium dioxide), even under mild plasma conditions with low-energy (<20 eV) ions. Using vertical trench nanostructures and microscopic cavity structures that locally block the flux of ions, it is observed that the impact of (low-energy) ions is an important factor for the TiO₂ film conformality. Specifically, it is demonstrated that the GPC in terms of film thickness can increase by 20% to >200% under the influence of ions, which is correlated with an increase in film crystallinity and an associated strong reduction in wet etch rate (in 30:1 buffered HF). The magnitude of the influence of ions is observed to depend on multiple parameters such as the deposition temperature, plasma exposure time, and ion energy, which may all be used to minimize or exploit this effect. For example, a relatively moderate influence of ions is observed at 200 °C when using short plasma steps and a grounded substrate, providing a low ion energy dose of ~1 eV nm² cycle⁻¹, while a high effect is obtained when using extended plasma exposures or substrate biasing (~100 eV nm² cycle⁻¹). This work on TiO₂ shows that detailed insight into the role of ions during plasma ALD is essential for precisely controlling the film conformality, material properties, and process reproducibility.

In this work, we studied the impact of ions on the growth of TiO₂ thin films by plasma ALD. This was done using microscopic cavity structures, which locally blocked the flux of ions during deposition. The results were analyzed by reflectometry, spectroscopic ellipsometry (SE) and Raman spectroscopy. In this document, we provide additional supporting data, namely: 1) an overview of the measured TiO₂ thickness profiles, 2) the wet etch rate data for TiO₂ grown with substrate biasing, 3) Raman spectroscopy data for TiO₂ grown at 200 °C using different plasma exposure times, and 4) scanning electron microscopy (SEM) images of the TiO₂ surface. Moreover, further details are given on how the SE data and Raman spectroscopy data were processed. But first, an overview is provided of growth per cycle (GPC) values reported in the literature for the studied process, suggesting an apparently low reproducibility.
1) LITERATURE: GPC values reported for plasma ALD of TiO$_2$ using Ti(NMe$_2$)$_4$

Figure S1 gives an overview of GPC values reported in the literature for ALD of TiO$_2$ using Ti(NMe$_2$)$_4$ and O$_2$ plasma or O$_2$/Ar plasma (see references below). A large spread in values is observed, suggesting that reproducibility is an issue for this process and presumably for ALD of TiO$_2$ in general. Several factors could contribute to this large spread, such as precursor decomposition at high temperatures$^1$ or a thermal growth component during the plasma step.$^2$ Yet, the influence of ions, which is illustrated by the GPC values obtained in this work with exposure to ions (solid circles) and without any contribution of ions (open circles), is expected to be one of the dominant factors behind the apparently limited reproducibility. This exemplifies that detailed insight into the influence of ions during plasma ALD of TiO$_2$ is vital.

![Figure S1: Values of the GPC (in terms of film thickness) for plasma ALD of TiO$_2$ using Ti(NMe$_2$)$_4$, as reported in the literature (squares) and as obtained in this work with exposure to ions (solid circles) and without exposure to ions (open circles). The values are plotted against the reported setpoint temperature, which may deviate from the exact substrate temperature. For clarity, the measurement uncertainties and the influence of plasma exposure time (observed in this work) are omitted.](image)

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2) REFLECTOMETRY: Measurement thickness profiles and overview data

To study the influence of ions, the TiO$_2$ films were grown on lateral-high-aspect-ratio (LHAR) cavity structures (PillarHall® generation 4),$^{3,4}$ where only part of the surface was exposed to ions.$^5$ Subsequently, the local thicknesses of the deposited films were mapped by optical reflectometry, using a Filmetrics F40-UV with a StageBase-XY10-Auto-100mm mapping stage. The thicknesses were fitted from the interference pattern (i.e., reflected light intensity versus wavelength) assuming a refractive index of 2.49 at 633 nm of the TiO$_2$ film, as verified by SE. The assumption of a constant refractive index is not perfect, but has a relatively limited effect on the accuracy of the measured GPC. A selection of thickness profiles was given in the main text of this work. Here, in Figure S2, we provide the thickness profiles obtained using different plasma exposure times, that were used to determine the GPC values reported in Figure 7 of the main text.

In addition to the reflectometry measurements, the thicknesses and refractive indices of the films grown with exposure to ions were measured by spectroscopic ellipsometry. These measurements were performed on pieces of silicon wafer that were processed alongside the corresponding LHAR structure. Further details on the used SE model are provided in Section 4 of this document. Figure S2 shows that the reflectometry data obtained in the ion-exposed regions of the LHAR structures (shaded area) are consistent with the SE measurements (horizontal bars), within an uncertainty of 0.075 Å/cycle. Moreover, the impact of ion exposure on the GPC, as discussed in the main text, is clearly visible.
Figure S2: Local GPC of TiO$_2$ films grown on LHAR cavity structures (using 400 ALD cycles) at temperature setpoints of 100, 200 and 300 °C, indicating a significantly higher GPC in the region where the TiO$_2$ is grown with exposure to ions (left). The GPC and wet etch rate values obtained with exposure to ions are confirmed by spectroscopic ellipsometry (horizontal bars).

3) REFLECTOMETRY: Measurement wet etch rate and data for TiO$_2$ grown with substrate biasing

Optical reflectometry was also used to measure the local wet etch rate of the deposited TiO$_2$. This was done by measuring the thickness profiles, as plotted in Figure S2, before and after partly etching the films in 30:1 buffered hydrofluoric acid (BHF) at room temperature, with NH$_4$F as the buffer agent. The differences in film thickness were divided by the etch time (420 seconds in this work) to obtain the local wet etch rates as plotted in Figure 6 of the main text. To avoid any variation in etching conditions, the wet etch rate profiles reported in the main text were obtained by simultaneously etching the films in one BHF dip.

Here, in Figure S3, we provide the wet etch rate profile measured for the TiO$_2$ film grown at 200 °C using 60 W substrate biasing (~120 eV mean ion energy) and plasma steps of 12 s. As a benchmark, the wet etch rate (determined using the same BHF dip) is also plotted for the film grown at 200 °C using a grounded substrate (9±1 eV mean ion energy) and plasma steps of 38 s. Similar to the results reported in the main text, for both samples no significant etching is observed in the ion-exposed region. Moreover, the wet etch rate in the ion-shielded region is comparable for the TiO$_2$ grown with and without substrate biasing. This is as expected, since substrate biasing, and as a result high ion energies, should have no significant influence on the film grown in the ion-shielded region. It is noted that for the data given in Figure S3 a different, potentially contaminated, 30:1 BHF solution was used compared to the measurements provided in the main text, giving somewhat lower wet etch rate values. Moreover, for the data given in Figure S3 the film grown without substrate biasing was etched for the second time, which may have influenced that particular measurement.
Figure S3: Local wet etch rate of TiO$_2$ films grown at 200 °C using 60 W substrate biasing and plasma steps of 12 s (black stars) and using a grounded substrate and plasma steps of 38 s (orange circles). This data was obtained in a separate experiment compared to the results reported in the main text, giving slightly different wet etch rate values.

4) SPECTROSCOPIC ELLIPSOMETRY: Optical model and fitted data

As mentioned in Section 2 of this document, the thicknesses of the films grown with exposure to ions were verified by spectroscopic ellipsometry (SE). Moreover, SE was used to determine the refractive indices of these films. The SE measurements were performed ex-situ, using a M–2000D Spectroscopic Ellipsometer of J.A. Woollam Co., on pieces of silicon wafer that were processed alongside the corresponding LHAR structure (Czochralski silicon (100), single side polished, ~1.6 nm native oxide).

The angles $\Psi$ and $\Delta$, which express the change in polarization of the light beam upon reflection on the sample (i.e., the amplitude ratio $\tan \Psi$ and phase angle $\Delta$),$^6$ were measured for a photon energy range of 1.24 eV up to 6.5 eV. An example of an SE measurement is given in Figure S4. In all measurements, the raw data (gray squares) were fitted using the CompleteEASE v5.10 software of J.A. Woollam Co., according to a B-Spline model (solid lines). A B-Spline model was adopted such that the dielectric function of the film could be fitted for the full photon energy range, including the bandgap. Furthermore, the (partly) crystalline TiO$_2$ films grown at 200 and 300 °C were modelled as a graded layer, where the dielectric function was either higher or lower (by <5%) at the bottom of the film compared to the top of the film.
Figure S4: Example of experimental SE data (gray squares) and modelled data (solid lines) for a TiO$_2$ film grown with exposure to ions, using a temperature setpoint of 200 °C, a grounded substrate and plasma steps of 12 s.

An overview of fitted dielectric functions is provided in Figure S5. Here, $\epsilon_1$ and $\epsilon_2$ are the real ($\epsilon_1$) and imaginary ($\epsilon_2$) parts of the complex dielectric function $\epsilon = \epsilon_1 + i\epsilon_2$. These are related to the refractive index $n$ and extinction coefficient $k$ according to $\epsilon_1 = n^2 - k^2$ and $\epsilon_2 = 2nk$. It is observed that under all conditions the optical bandgap, which is related to the energy at which $\epsilon_2$ starts to rise,$^6,8$ remains approximately constant. In contrast, the magnitude of $\epsilon$ is influenced by the deposition temperature and plasma exposure time. Specifically, at 100 and 200 °C the dielectric function tends to increase with plasma exposure time, which is attributed to the influence of ions (see Figure 7 of the main text).

Figure S5: Dielectric functions fitted for the TiO$_2$ films grown with exposure to ions (on Si reference samples, using 400 ALD cycles) at temperature setpoints of 100, 200 and 300 °C.
5) RAMAN SPECTROSCOPY: Data processing procedure and the effect of plasma exposure time

In the main text of this work, substrate-corrected Raman spectra of the deposited TiO$_2$ films were shown and discussed, which were measured using an Invia confocal Raman microscope of Renishaw. Here, we illustrate how these substrate-corrected spectra were obtained from the raw measurement data. Furthermore, we provide the substrate-corrected Raman spectra obtained at a temperature setpoint of 200 °C using different plasma exposure times. To quantitatively compare the different Raman measurements, all measured spectra were normalized to the 302 cm$^{-1}$ peak of the silicon substrate (i.e., the all-silicon PillarHall® LHAR structure). Figure S6 shows examples of normalized spectra, measured for the bare substrate (black) and for the substrate with deposited TiO$_2$ film (blue). The difference between the two normalized spectra gives the substrate-corrected spectrum of the deposited film (red).

![Normalized spectra](image)

*Figure S6: Raman spectra measured for a bare silicon substrate (black) and for a silicon substrate with deposited TiO$_2$ film (blue). Both spectra are normalized to the 302 cm$^{-1}$ peak of the silicon substrate (indicated by the dotted line). The difference between these normalized spectra gives the substrate-corrected spectrum of the deposited film (red), as presented in this work.*

In the example of Figure S6, the substrate-corrected spectrum corresponds to the TiO$_2$ film grown with exposure to ions, using a temperature setpoint of 200 °C, a grounded substrate and plasma steps of 38 s. Peaks corresponding to the anatase phase of TiO$_2$ are visible at 144, 394 and 634 cm$^{-1}$, indicating that predominantly crystalline TiO$_2$ was grown at these conditions. Figure S7 shows that the same holds for the depositions done using different plasma exposure times (of 3.8, 12, 21 or 120 s per cycle), although the areas of the peaks tend to be higher when using longer plasma exposures. This suggests that the crystallinity of the TiO$_2$ (i.e., the fraction of crystalline material and/or the average crystal size) increases with the plasma exposure time employed.
Figure S7: Substrate-corrected Raman spectra measured for the TiO$_2$ films grown at 200 ºC, with exposure to ions, using a grounded substrate and plasma exposure times of 3.8, 12, 21, 38 or 120 s per cycle.

The increase in film crystallinity observed in Figure S7 is attributed to the impact of ions, where a higher impact is obtained when supplying a higher dose of ions. This behavior is further exemplified in Figure S8, showing data for the films grown at 200 ºC with exposure to ions (solid datapoints) and without any contribution of ions (open datapoints). Panel (A) gives the refractive index (at 633 nm or 1.96 eV), panel (B) the area of the substrate-corrected Raman peak at 144 cm$^{-1}$ and panel (C) the average GPC over 400 cycles.

Figure S8: Refractive index (A), area of the Raman peak at 144 cm$^{-1}$ (B) and GPC (C) of the TiO$_2$ films grown at 200 ºC using a grounded substrate, with exposure to ions (solid datapoints) and without exposure to ions (open datapoints).
With exposure to ions, the refractive index, Raman peak area and GPC plotted in Figure S8 all tend to increase when using longer plasma steps. Deviations of the overall trend may be related to sample-to-sample variations which can be caused by slight differences in processing conditions, such as the chamber conditioning and thermal contact with the table. In contrast, without exposure to ions the Raman peak area remains negligible, suggesting an amorphous film, and the GPC remains approximately constant around 0.63 Å/cycle.

6) SCANNING ELECTRON MICROSCOPY: Images of the TiO$_2$ surface

Finally, in this section we provide top-view SEM images (recorded by a JSM-7500FA high-resolution SEM of JEOL) of the TiO$_2$ films grown at temperature setpoints of 100, 200 and 300 °C, using a grounded substrate and plasma steps of 38 s. The images are given in Figure S9, where the area left of the dotted line corresponds to the surface area that was exposed to ions during deposition, while the surface area at the right was shielded from ions. Note that the ion-shielding membrane of each LHAR structure (illustrated in the top image) was removed in these images. As further discussed below, differences in surface morphology (although not clearly visible) can be observed.

The top image displays the film grown at 100 °C, which appears to have a relatively smooth surface in the region where the film was grown with exposure to ions (left) and without exposure to ions (right). Since a rough, faceted surface is expected for crystalline TiO$_2$, this suggest that the film grown at 100 °C is predominantly amorphous in both regions. In contrast, the film grown at 200 °C appears to have a faceted surface in the ion-exposed region, while a relatively smooth surface is obtained in the ion-shielded region. This indicates that, at 200 °C, crystalline TiO$_2$ was grown only with exposure to ions. Finally, the film grown at 300 °C exhibits a rough surface in both regions, indicating that film crystallization was also obtained without exposure to ions. These observations are all in line with the Raman spectroscopy data measured for these samples (see Figure 6 of the main text).
Figure S9: Top: schematic cross-sectional side view of a LHAR structure used to study plasma ALD of TiO$_2$ with (left) and without (right) exposure to ions. Below: top-view SEM images of the structures after deposition of TiO$_2$ and removal of the membrane. The films were grown using 400 cycles, a grounded substrate, plasma steps of 38 s and temperature setpoints of 100, 200 and 300 °C.
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