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FULL PAPER

TiO₂ thin film patterns prepared by chemical vapor deposition and atomic layer deposition using an atmospheric pressure microplasma printer

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Abstract
A microplasma printer is employed to deposit thin film patterns of TiO₂ by titanium tetra-isopropoxide and N₂/O₂ plasma at atmospheric pressure. The setup is adopted to carry out deposition in two configurations, namely under chemical vapor deposition (CVD) and atomic layer deposition (ALD) modes. The properties of TiO₂, as well as the patterning resolution, are investigated. The amorphous TiO₂ deposited in the CVD mode contains a relatively high level of impurities (residual carbon content of 5–10 at.%) and is characterized by a low refractive index of 1.8. With the ALD mode on the other hand, TiO₂ is obtained with a low level of impurities (<1 at.% C and <2 at.% N), a refractive index of 1.98, and a growth per cycle of 0.15 nm. Furthermore, the spatial resolution for a 8 nm-thick film is determined by X-ray photoelectron spectroscopy line scan and found to be equal to 2,000 and 900 µm for the CVD and ALD modes, respectively. This study can be regarded as the first step toward area-selective CVD and ALD of TiO₂ by a microplasma printer, which can be further explored and extended to other material systems.

KEYWORDS
plasma-assisted atomic layer deposition, plasma printing, titanium dioxide

1 | INTRODUCTION

Direct deposition of thin film patterns has recently become a subject of extensive research.¹,² Many areas ranging from semiconductor to biomedical applications require fabrication of patterned microstructure and nanostructures.³–⁵ Besides applications which require nanoscale patterns, a broad range of devices such as thin film transistors (TFTs),¹⁶–⁷ solar cells,¹⁸ sensors,¹⁹ and microfluidic channels¹⁰,¹¹ demand micron-scale patterns in their structures. The fabrication of some of these devices relies on costly patterning methods, such as (photo-)lithography. Therefore, alternative, simple, and cost-effective approaches, from submillimeter to micron-scale patterning, are sought.

Chemical vapor-based thin film deposition techniques such as chemical vapor deposition (CVD) and
atomic layer deposition (ALD) have been both acknowledged for delivering thin films with accurate control in chemical, opto-electrical, and structural properties.\textsuperscript{[12,13]} Fabricating patterns of thin films by CVD and ALD is generally achieved either by top-down or bottom-up approaches.\textsuperscript{[2]} The former involves either masking selected areas of the substrate with a resist followed by thin film deposition and mask removal (lift-off), or masking selected areas of deposited film with a resist followed by etching and subsequent mask removal. The bottom-up approach instead does not require the masking step, and patterning is mainly achieved via local activation of the desired areas of the substrate to promote film growth only on those selected areas. Bottom-up processes, which rely on the inherent properties of materials to allow for selective deposition, are desired due to the fewer processing steps.\textsuperscript{[14–16]} Furthermore, they allow for self-aligned fabrication of patterns that can address the alignment challenge associated to top-down approaches.\textsuperscript{[17,18]} Hence, there is currently a large interest in such bottom-up approaches for area-selective deposition.\textsuperscript{[17,19]} As an example, nanoscale patterning of metals on oxides was shown by depositing a seed layer of Pt with electron beam-induced deposition before Pt ALD.\textsuperscript{[20]} Pt ALD growth instantly occurs on Pt seed layer, while Pt seed-free oxide regions experience a long incubation time for Pt growth. Another example of a bottom-up process is submillimeter scale patterning of In\textsubscript{2}O\textsubscript{3}:H using local plasma activation of H-terminated Si surface, before ALD.\textsuperscript{[21]} The latter benefits from the selective growth of In\textsubscript{2}O\textsubscript{3}:H with InCp precursor and H\textsubscript{2}O/O\textsubscript{2} mixture on oxidized Si surfaces.\textsuperscript{[22]} In both examples of area-selective ALD, ALD growth is promoted on the activated areas, while ALD growth on the other regions experiences an incubation time. It is important to note that these bottom-up approaches require at least two processing steps (local activation and subsequent ALD) and rely on the ALD precursor’s chemistry and precursor/substrate combination.

In this contribution, we introduce a one-step patterning approach for thin oxide films based on a microplasma printer: the film can be directly deposited on selected areas of the substrate according to a pattern defined through software. Specifically, the microplasma printer, which is a multi-needle-to-plate dielectric barrier discharge (DBD) system, enables a dot-wise plasma ignition on the surface. The microplasma printer was originally adopted for surface treatment and functionalization using nondepositing gases such as N\textsubscript{2}/O\textsubscript{2} mixtures.\textsuperscript{[23,24]} An example of patterning application was already mentioned above: a novel two-step process for submillimeter scale area-selective ALD of transparent conductive oxides by activation of H-terminated Si using a microplasma printer before In\textsubscript{2}O\textsubscript{3}:H deposition by ALD.\textsuperscript{[21]} Hexamethyldisiloxane (HMDSO) and (3-aminopropyl)trimethoxysilane (APTMS) were also tested as precursors in the microdischarge area. Plasma-polymerized HMDSO was applied to generate hydrophobic surfaces,\textsuperscript{[25]} and APTMS was adopted to deliver amine functionalities at the surface, followed by subsequent metal electrodeless nickel plating.\textsuperscript{[26]}

Whereas the microplasma printer has proven its robustness primarily in patterned surface functionalization, its potential in delivering patterned, ultra-thin oxide films in only one step has not been explored yet. More specifically, in this study, we present the first step toward such a one-step patterning of thin oxide films by a microplasma printer, by addressing the case study of TiO\textsubscript{2}. This material has been chosen because it has been already widely investigated in different CVD and ALD processes. In more detail, we adopt the atmospheric pressure microplasma source in two configuration modes. The first features plasma activation of both precursor (titanium tetra-isopropoxide [TTIP]) and N\textsubscript{2}/O\textsubscript{2} mixtures, according to a plasma-enhanced CVD mode. The second features plasma activation of only N\textsubscript{2}/O\textsubscript{2} mixtures, following the exposure of the substrate to the Ti-precursor, according to a plasma-enhanced ALD mode.

The paper is organized as follows. The Section 2 addresses the hardware modifications necessary to run the microplasma setup in the two deposition modes, as well as the materials and characterization methods used. The Section 3 presents the discussion of the TiO\textsubscript{2} film characterization when deposition is carried out in the two modes, CVD and ALD. Finally, we also discuss the outcome of the first spatial resolution studies when TiO\textsubscript{2} is deposited in CVD and ALD modes, by means of X-ray photoelectron spectroscopy (XPS) line scan measurements. The Section 4 of this study are presented at the end.

2 | EXPERIMENTAL SECTION

2.1 | Microplasma printer

The microplasma printer (InnoPhysics B.V., Eindhoven, the Netherlands)\textsuperscript{[23,26]} is a multi-needle-to-plate DBD system operating at atmospheric pressure (Figure 1). It can operate in air, but a controlled N\textsubscript{2}/O\textsubscript{2} mixture was adopted in this study. A high voltage AC power source with an operating frequency of 60–70 kHz is used as power supply and connected to the printer table. The plasma is generated between the table and grounded printing head with a dielectric layer placed in the gap.
between the electrodes. The exact position of the dielectric layer depends on the substrate material. If the substrate is nonconductive, the substrate itself can serve as a dielectric and there is no need for an extra dielectric layer (Figure 1d-left). In case of (semi-) conductive substrate, a 260-µm-thick Al₂O₃ sheet acts as dielectric between the needles and substrate. The plasma is generated on both sides of the dielectric sheet between the electrodes. In every single plasma printing step which is defined as 1 print repeat (PR), the print head is moved with a constant speed (10–60 mm/s) over the substrate surface while the needle electrodes are actuated only on the areas of the substrate which are predefined by the software. The average time for which each area of the substrate is exposed to the plasma with the above-mentioned voltage and interelectrode gap distance is independent of the head speed and is 400 µs. Therefore, 1 PR in this paper is equivalent to 400 µs of plasma.

2.2 Thin film deposition by microplasma printer

The microplasma printer was adapted for operating according to two deposition modes, CVD and ALD of TiO₂. The two different designs of the chamber are reported in Figure 2. In the CVD design, precursor and plasma gas were injected simultaneously to the front of the needle electrodes and an exhaust line was placed behind the needle electrodes. While in the ALD design, precursor injection was separated from the plasma needles and plasma gas by means of a N₂ curtain. In both cases, the chamber was protected against ambient air and moisture by means of a N₂ curtain ring with a flow of 2 slm during the process. The N₂ used had a purity of 99.999%. TTIP (≥97% purity; Sigma Aldrich) was used as the CVD and ALD precursor and was heated to 30°C. N₂ was used as carrier gas. Stainless steel flexible lines carrying the precursor were heated to 50°C to prevent vapor condensation. The substrate table was also heated to 60°C.

2.2.1 Plasma-enhanced CVD

Silicate glass (Menzel-Gläser; Thermo Scientific) and p-type c-Si (100) wafers were used as the substrates for CVD process. Depositions on c-Si were performed with just injecting TTIP carried by 53 sccm N₂ to the plasma. While for deposition on glass, TTIP was carried by 25 sccm N₂ and mixed with 0–10 sccm of O₂ (99.999%) before being injected to the plasma. To have sufficient area for analysis, a rectangle TiO₂ film with an area of 3.3 × 12 mm² was deposited on each substrate. By using a digital pattern, the distance between each plasma spot was set to 90 µm to avoid thickness nonuniformity along the deposited films.

2.2.2 Plasma-enhanced ALD

p-Type c-Si (100) wafer was the substrate for the ALD process by the microplasma printer. The O₂ plasma generated by the microplasma was used as a coreactant,
and the substrate was exposed to TTIP (carried by 25 sccm N\textsubscript{2}) and O\textsubscript{2} plasma by moving the head back and forth between two areas spatially separated by a N\textsubscript{2} gas flow (Figure 2b\textsubscript{1} and b\textsubscript{2}). It is noteworthy that the constant flow of O\textsubscript{2} (10 sccm) mixed with the N\textsubscript{2} from curtain gas such that a N\textsubscript{2}/O\textsubscript{2} plasma was generated. TTIP was supplied continuously and its exposure time was varied between 315 and 1,900 ms by tuning the speed of the head. Depending on the exposure time, purge time was varied between 650 and 3,900 ms. The precursor exposure and purge time for different head translation speeds are presented in Table S1. In some cases, a purge time step was added between the plasma and TTIP exposures by holding the substrate in the plasma region (plasma off), which is referred here to as “extra purge time.” The plasma exposure time in every PR was calculated to be 400 µs for the given voltage and gap distance between the electrodes in this study and was independent of both TTIP exposure and purge times. To increase the plasma exposure time, the number of PRs in each ALD cycle was increased. The distance between TTIP exposure and plasma region was large enough (compared to the deposition area) to avoid multiple exposure of the substrate to TTIP when several PRs were performed in every ALD cycle. Similar to the CVD mode, in ALD mode also, a rectangle TiO\textsubscript{2} film with an area of 3.3 × 12 mm\textsuperscript{2} was deposited on each substrate to allow for film analysis. For resolution study in Section 3.3, two needle electrodes were used in the ALD mode to facilitate the N\textsubscript{2}/O\textsubscript{2} plasma ignition. This was because the plasma generated in N\textsubscript{2}/O\textsubscript{2} was less stable with only one needle. To ignite the plasma with the same voltage and O\textsubscript{2} flow rate as the deposition with all needle electrodes (5.8 kV, 10 sccm O\textsubscript{2}) and have a stable plasma, two needle electrodes were necessary.

### 2.3 Thin film characterization

The thickness and refractive index (n) of the films were measured on c-Si and glass substrates by a variable angle spectroscopic ellipsometer (M-2000D; J. A. Woollam Inc.) employing a Tauc-Lorentz model in the wavelength range of 300–1,000 nm for analysis. Moreover, for the PECVD films, the optical model included an effective medium approximation (EMA) layer to take into account the film surface roughness. This layer consisted of 50% voids and 50% of the bulk film. Consequently, half of the EMA layer was added to the bulk film thickness to determine the whole film thickness. Errors in the thicknesses and growth rates were determined from several spectroscopic ellipsometry measurements on every sample. Top-view images of the deposited films were recorded by a field emission scanning electron microscope (Sigma, Zeiss) with an accelerating voltage of
2 kV. Atomic force microscopy (AFM, Dimension 3100; Veeco) was used to visualize the surface morphology of the films. AFM raw data were processed by the open source software Gwyddion. XPS measurements were carried out on the as-deposited samples and after 60 s of sputtering with low energy (500 eV) Ar+ to remove adventitious carbon from the surface. The binding energy values were corrected for charging, based on the C1s peak at 284.7 eV, associated to surface contamination upon exposure of the film to ambient. For XPS line scans, the diameter of the X-ray beam was reduced from 400 to 50 µm and the distance between two consecutive measurements was set at 60 µm. Rutherford backscattering spectrometry (RBS) and elastic recoil detection (ERD) were performed for measuring the atomic composition of TiO$_2$ films by ACCTEC B.V. spectrometer using a 1,900 keV He$^+$ beam. During RBS measurements, detectors were at scattering angles of 140° and 170°. The detector was at a recoil angle of 30° for ERD measurements. To identify any possible crystalline structure in the TiO$_2$ films deposited on the small area, Raman spectroscopy was performed with a Renishaw spectrometer (Renishaw) using a 514 nm laser as the excitation source.

3 | RESULTS AND DISCUSSION

3.1 | Atmospheric pressure plasma-enhanced CVD of TiO$_2$

The atmospheric pressure plasma-enhanced CVD of TiO$_2$ films was performed on glass substrates by flowing TTIP with and without O$_2$. The same was done on c-Si but in this case by flowing only TTIP to the chamber as due to physical limitations of the hardware, depositions on c-Si substrate could only be done without adding O$_2$. Figure 3 shows increase in thickness of TiO$_2$ layers as a function of the number of PRs. The thickness of the TiO$_2$ film on glass substrate was measured to be 56 nm after 25 PRs when only TTIP was injected into plasma. The growth rate can be calculated per plasma repeat, equivalent to a plasma duration of 400 µs. Hence the growth of 2.2 ± 0.2 nm/PR corresponds to a growth rate of 5.5 nm/ms on glass substrate in the absence of O$_2$. The growth decreased to 1.9 ± 0.2 nm/PR (growth rate is 4.7 nm/ms) by adding 10 sccm of O$_2$ to the gas mixture. In case of deposition on c-Si, the growth was 1.3 ± 0.1 nm/PR (growth rate is 3.25 nm/ms). The decrease in growth rate by adding O$_2$ when deposition was performed on glass can be ascribed to formation of O radical in the N$_2$/O$_2$ plasma leading to more efficient abstraction of hydrocarbon ligands from TTIP, as addressed later when discussing the film chemical composition. The lower growth rate achieved in the case of c-Si substrates compared to glass was attributed to the difference in the DBD configuration (Figure 1), more specifically the difference in terms of interelectrode gap. The gap between two electrodes when deposition was performed on c-Si substrate (Figure 1d—right) was twice as the gap in the case of glass substrate (Figure 1d—left). Our experiments showed that a higher gap distance (more than 150 µm) in the microplasma DBD system led to lower energy density when keeping operating voltage the same (Figure S1a). Furthermore, there is a difference in dielectric material when depositions were carried out on glass and c-Si substrates. In case of depositions on glass, the 1-mm-thick glass substrate itself served as the dielectric role in DBD. While in case of depositions on c-Si, a 260 µm Al$_2$O$_3$ sheet was used as the dielectric in the gap between needle electrodes and table. The thickness and permittivity of the dielectric are known to have a strong effect on the properties of the plasma.\cite{27} It is also noteworthy that in all cases, the film growth during the first few PRs seem to be slightly different from the growth rate in the steady state regime (around ≥15 PR). This can be attributed to the difference in DBD behavior on various surfaces (glass and c-Si) at the initial stages versus TiO$_2$ during the steady state growth.

\footnote{There was no room to introduce an O$_2$ line due to the presence of the alumina sheet between the needles and the c-Si substrate.}
The plasma-enhanced CVD TiO2 films were amorphous, as no peaks related to anatase or rutile structures were found in their Raman spectra. The top-view scanning electron microscopy (SEM) images of around 80-nm-thick TiO2 films on glass are shown in Figure 4. The TiO2 films deposited with dosing only TTIP in the plasma (Figure 4a,b) were rough with particle-like features on top of TiO2 surface. A decrease in size of the features was observed when the applied voltage was increased from 4.8 to 5.8 kV. The morphology of the TiO2 film deposited by adding 10 sccm O2 to TTIP (Figure 4c) markedly changed toward less and smaller particles when compared to those TiO2 films deposited with only TTIP and with the same applied voltage. The morphology of the surface in Figure 4c, which is the sample deposited by TTIP and 10 sccm O2, is very similar to that observed by Yoshiki and Mitsui,[28] where TiO2 films were deposited by a mixture of TTIP with He/O2 plasma at atmospheric pressure.

The SEM observation was supported by AFM analysis. AFM micrographs of different TiO2 films deposited on glass and c-Si are displayed in Figure 5. AFM images of TiO2 films deposited on glass with only TTIP and two different applied voltages (Figure 5a,b) revealed smaller features for the sample deposited using higher plasma energy. The root mean square (RMS) value decreased from 18 ± 1 to 11 ± 1 nm by increasing the voltage from 4.8 to 5.8 kV. However, both samples appear to be affected by macro-porosity (shown by arrows in Figure 5a,b). The RMS value decreased to 4.0 ± 0.5 nm after adding 10 sccm O2 to the gas mixtures (Figure 5c), in line with the SEM image of the same sample (Figure 4c). Note that the RMS roughness of the bare glass substrate was 0.30 ± 0.05 nm. The sample deposited on c-Si substrate in the absence of O2, instead, was found to be smooth with an RMS value of 0.25 ± 0.05 nm (Figure 5d) similar to the RMS value of bare c-Si substrate itself. The contrast in the roughness of TiO2 films deposited on c-Si and glass substrates can be likely explained by the difference in charge distribution on conductive and dielectric surfaces in atmospheric pressure electric discharges. Deposited charge on the surface of a dielectric is known to be nonuniform.[29] Increasing the surface conductivity can result in a more uniform distribution of charges over the surface and therefore to an enhancement in stability and uniformity of plasma.[30] It should be noted that regardless of the process gas and deposition conditions, depositing smooth TiO2 layers in a DBD system has been reported to be a general challenge in the literature.[31,32]

The chemical composition of TiO2 layers deposited on glass and c-Si substrates was determined by XPS and is presented in Table 1. The TiO2 films were deposited on glass using 25 sccm of TTIP and different applied voltages and O2 flows, while the TiO2 film on c-Si was deposited with 53 sccm of TTIP. For depositions on glass with only TTIP, TiO2 films contained around 10 and 3 at.% of C and N, respectively, and increasing the voltage from 4.8 to 5.8 kV did not lead to further changes in layer chemical composition. Adding 5 and 10 sccm O2 to the plasma resulted in a gradual decrease in the C content from 10.1 at.% to <5% and in N content from 3.4% to 1.7%, respectively. Increasing the amount of O2 in the plasma leads to generation of O radicals which can combust the TTIP fragments.[33] However, the chemistry of TTIP/O2/N2-fed plasma can be more complicated and the presence of other oxidizing agents such as O3 and NOx in the plasma cannot be excluded. In fact, Fourier transform infrared (FTIR) analysis confirmed the presence of O3 and different types of NOx in the effluent gas of the N2/O2-fed microplasma (Supporting Information).

In case of TiO2 films grown on c-Si substrates, the C content was found to be lower than in the case of glass substrates and the amount of N was negligible (Table 1). The lower amount of N could be due to the lower energy density under higher interelectrode gap conditions and
limited atomic N formation by direct electron impact dissociation. Yet the refractive index \((n)\) of a 50-nm-thick film on c-Si substrate was \(1.8 \pm 0.05\) at 632.8 nm, which is much lower than the typical value for dense and amorphous TiO\(_2\) film \((n = 2.2–2.4)\).\(^{[34]}\) The lower refractive index of the plasma-enhanced CVD TiO\(_2\) films in this study compared to dense TiO\(_2\) can be related either to the residual carbon in the film or presence of porosity in the layers.

XPS scans of Ti2p and N1s spectral regions were used to identify the chemical bonds in plasma-enhanced CVD TiO\(_2\) films (Figure 6). Ti2p\(_{3/2}\) and Ti2p\(_{1/2}\) peaks

\[\text{TABLE 1} \quad \text{XPS analysis of the CVD TiO}_2 \text{ films deposited on glass and silicon with different flows of O}_2 \text{ in the gas mixture and different applied voltages}\]

| Gas composition | Substrate | Voltage (kV) | Atomic % |
|-----------------|-----------|-------------|----------|
|                 |           |             |          |
| 25 sccm TTIP    | Glass     | 4.8         | 10.1     | 3.2     |
| 25 sccm TTIP    | Glass     | 5.8         | 10.7     | 3.4     |
| 25 sccm TTIP + 5 sccm O\(_2\) | Glass     | 5.8         | 6.8     | 1.7     |
| 25 sccm TTIP + 10 sccm O\(_2\) | Glass     | 5.8         | 4.9     | 1.7     |
| 53 sccm TTIP    | c-Si      | 5.8         | 7.5     | <1      |

Note: The values are reported after 60 s of sputtering with Ar ions to remove the surface C contamination. The maximum error in the elemental concentration measured by XPS was 0.5%. The thickness of the samples was in the range of 20–40 nm.

Abbreviations: CVD, chemical vapor deposition; TTIP, titanium tetra-isopropoxide; XPS, X-ray photoelectron spectroscopy.

\[\text{FIGURE 5} \quad \text{Atomic force microscopy images of chemical vapor deposition TiO}_2 \text{ films prepared with 40 PR on glass and c-Si substrates under various conditions in terms of voltage and gas mixture. (a) 4.8 kV, on glass substrate with only titanium tetra-isopropoxide (TTIP), (b) 5.8 kV, on glass substrate with only TTIP, (c) 5.8 kV, on glass substrate with TTIP and 10 sccm O}_2\text{, (d) 5.8 kV, on c-Si substrate with only TTIP. Black arrows in (a) and (b) are pointing to "macroporosity" in the film. The thickness of the film on the glass substrate is around 80 nm and on c-Si is 52 nm.}\]

\[\text{FIGURE 6} \quad \text{High-resolution (a) Ti2p and (b) N1s X-ray photoelectron spectroscopy spectra of chemical vapor deposition TiO}_2 \text{ films using only titanium tetra-isopropoxide on glass and c-Si substrates.}\]
associated to the layer deposited on c-Si were found at 459.1 and 464.9 eV, respectively, which correspond to the Ti$^{4+}$ oxidation state. The peaks were shifted to lower binding energy values by 0.6 eV when analyzing TiO$_2$ on glass. The shift can be explained by the presence of Ti–N–O bonds in the film, confirmed by the N1s peak at 401.5–402 eV, observed for the TiO$_2$ films deposited on glass.[35,36] The peak at 400 eV can be assigned to molecularly adsorbed nitrogen such as NO$_x$.[36–38] N$_2$O$_y$ neutrals and charged species such as NO, NO$_2$, NO$_3$, N$_2$O$_5$, NO$^-$, NO$_2^-$, and NO$_3^-$ have been reported to form in N$_2$/O$_2$ DBDs,[39–41] and similar species were detected by FTIR in the effluent gas of the N$_2$/O$_2$-fed microplasma (Supporting Information). When O$_2$ was not employed, we hypothesize that oxygen could be incorporated (Table S2) in the film due to potential diffusion of air through the N$_2$ curtain. Further investigation is required to confirm this hypothesis.

To place our results in perspective, it is worth reporting that several DBD-enhanced TiO$_2$ deposition processes using TTIP combined with different gas mixtures (TTIP combined with Ar/N$_2$/O$_2$) were reported in the literature. Klenko and Pichal used a TTIP/Ar/O$_2$ mixture in a planar DBD and deposited carbon-rich TiO$_2$ layers.[31,42] They reported RMS roughness values between 15 and 23 nm for their TiO$_2$ films, which is in the range of values for the CVD TiO$_2$ films deposited on glass with the microplasma printer. More recently, Shelemin et al.[32] reported a process for depositing nitrogen-doped TiO$_2$ nanoparticles using TTIP/N$_2$/O$_2$ gas mixture in a planar DBD system. They studied the effect of gas flow rate, as well as plasma power on the chemical composition of the films and they observed a carbon content in the range of 15–39 at.%, which are much higher than the carbon levels of the films obtained through CVD by the microplasma printer (5–10 at.%). They also observed an increase in the amount of N in the film by increasing the gas flow rate to the discharge volume, while keeping the ratio between O$_2$ and N$_2$ constant. Hodgkinson et al.[43] reported C content of about 46 at.% for TiO$_2$ films deposited by TTIP at atmospheric pressure and using He as the carrier gas.

To summarize, we adopted several surface characterization techniques to evaluate the physical and chemical properties of the plasma-enhanced CVD TiO$_2$ films. It was found that the TiO$_2$ films were smooth only when deposited on c-Si. All films deposited on glass and c-Si contained C impurities and only those on glass contained N impurities. The chemical composition of the films was comparable to some of the plasma-enhanced CVD TiO$_2$ films (different process pressure and precursor) in the literature.[44,45] The films deposited by the CVD using the microplasma printer can be considered as a potential candidate for applications in which high density TiO$_2$ is not required, such as for example in certain gas-sensing applications[46,47] or as electrode in perovskite solar cells.[48]

### 3.2 Atmospheric pressure plasma-enhanced ALD of TiO$_2$

To explore the potential of the microplasma printer for area-selective ALD, the design of printing head was modified, as described earlier in Section 2.2. The saturation behavior and chemical composition of the films were investigated by analyzing the TiO$_2$ films locally deposited on c-Si in a simple rectangular shape.

#### 3.2.1 Saturation behavior

To verify the self-limiting ALD growth, saturation curves were obtained by varying the TTIP exposure and purge times. Figure 7a shows the growth per cycle (GPC) of...
TiO₂ layers as a function of TTIP exposure time for different purge times. The GPC increased to 0.15 nm and saturated at 475 ms of TTIP exposure and 30 s of extra purge time. As explained in Section 2, the extra purge time was carried out after both TTIP and plasma exposure by holding the substrate (deposition area in Figure 2b) in the plasma region. For shorter extra purge times, saturation of the growth rate was not achieved and increasing the TTIP exposure time led to an increase in GPC up to 0.35 nm for 2 s of TTIP exposure time and 0 s extra purge. The latter is attributed to a contribution of parasitic CVD reactions to film growth. Such CVD reactions can occur between unreacted TTIP and the gas species from the subsequent plasma exposure. Figure 7b shows the GPC of TiO₂ ALD as a function of extra purge time, when TTIP and plasma exposure time were 475 ms and 400 µs, respectively. For these conditions, saturation was achieved after 10 s of extra purge time. It is noteworthy that the TiO₂ films deposited by ALD in saturation conditions were smooth with RMS values of 0.25 ± 0.05 nm, according to the AFM measurements. Raman measurements also confirmed amorphous nature of the films deposited under the ALD mode.

The saturated GPC value obtained in this study (0.15 ± 0.05 nm) is within the range of GPC values reported in the literature (Table 2). The GPC value of ALD TiO₂ layers grown at low pressures and low temperatures (<100°C) with TTIP and O₂ plasma were reported to be between 0.05 and 0.19 nm when using different plasma sources and temperatures.⁴⁹,⁵⁴,⁵⁵ Plasma-enhanced ALD of titanium oxide at atmospheric pressure was reported by Theirich et al.⁵⁶ They used TTIP and Ar/O₂ plasma in a DBD reactor and obtained a GPC value of 0.16 nm. However, they pointed out that at least one fourth of the growth is CVD reaction-induced due to residual moisture in their reactor. For the ALD TiO₂ samples in this study, we calculated the number of deposited Ti atoms per ALD cycle based on RBS analysis, which resulted to be between 2.2 and 2.4 atom·nm⁻²-cycle. This is higher than what was reported for plasma-enhanced ALD of TiO₂ between 25°C and 250°C by Potts et al.⁴⁹,⁵⁰ that is between 0.9 and 1.5 Ti atom·nm⁻²-cycle and corresponding to a GPC of 0.05–0.06 nm. Other studies that obtained a higher GPC range (Table 2) did not provide information regarding the number of Ti atoms and therefore a direct comparison with their study in terms of the number of deposited Ti atoms per ALD cycle is not possible.

We hypothesize that the higher GPC of our study compared to some of the other studies in the literature can be attributed to diffusion of moisture through the nonoptimal curtain system during the print-head translation and hence contribution of CVD reactions to the overall deposition process. However, the higher GPC can also be attributed to the presence of reactive species other than O radicals in N₂/O₂ plasma. As mentioned in the previous section, O₃ and nitrogen oxide species (Supporting Information) are formed in N₂/O₂ plasma at atmospheric pressure which might play a role in the oxidation step of the ALD cycle. At low temperatures (<100°C), the GPC of TTIP/O₃ process was reported to be 0.01 nm,⁵⁴ and hence we can infer that the role of O₃ during ALD with the microplasma printer at 60°C is negligible. Nitrogen oxides such as NO₂ and NO₃ have been reported to have impact on the growth of different metal oxides during O₃-based ALD when O₃ is generated by DBD; addition of N₂ to the O₂ supply of the DBD (as O₃ generator for ALD) and generation of N₂O₃ species has shown to yield a higher GPC in HfO₂, ZrO₂, La₂O₃, and a lower GPC in Al₂O₃, O₃-based ALD processes.⁵⁷–⁵⁹ To our knowledge, nitrogen oxides have not been explored as oxidants in ALD of TiO₂ and hence their impact on the ALD growth of TiO₂ is not known.

To study the effect of plasma exposure time on TiO₂ growth, the GPC was measured for the samples deposited by varying only the number of plasma PRs.

| Pressure       | Plasma gas | Substrate temperature (°C) | GPC (nm/cycle) | References                        |
|----------------|------------|----------------------------|----------------|-----------------------------------|
| Low pressure   | O₂         | Room temperature           | 0.05–0.06      | Potts et al.⁴⁹                     |
|                | O₂         | 25–300                     | 0.06           | Potts et al.⁵⁰                     |
|                | O₂         | 100–400                    | 0.06–0.12      | Kang et al.⁵¹                      |
|                | O₂–N₂O     | 250                        | (O₂–) 0.035–(N₂O–) 0.059 | Choi et al.⁵²                   |
|                | Ar/O₂–H₂O  | 50–325                     | 0.04–0.05      | Xie et al.⁵³                      |
|                | Ar/O₂      | 80                         | 0.056          | Aghaee et al.⁵⁴                    |
|                | O₂         | 50                         | 0.19           | Niskanen et al.⁵⁵                  |
| Atmospheric pressure | Ar/O₂     | Room temperature           | 0.16           | Theirich et al.⁵⁶                  |
|                | N₂/O₂      | 65                         | 0.15           | This study                        |

Abbreviations: ALD, atomic layer deposition; TTIP, titanium tetra-isopropoxide.
in every ALD cycle (Figure 8), while keeping the rest of the deposition conditions the same. Increasing the number of plasma prints from 1 to 3 resulted in a decrease in the GPC from 0.18 to 0.15 nm. The higher GPC at 1 PR can probably be attributed to incomplete removal of hydrocarbons due to inadequate plasma exposure time. Increasing the number of plasma prints further to 10 did not result in any noticeable change in GPC; however, the chemical composition of the TiO₂ layers changed, as will be discussed in the next section.

3.2.2 | Chemical composition

The effect of plasma pulse length on C and N impurity content of TiO₂ films was studied via XPS and is presented in Table 3. The carbon and nitrogen content decreased from 5 and 3 at.% to <1 and 2 at.%, respectively, when the number of PRs increased from 1 to 7 in each ALD cycle. Despite the fact that the GPC already saturated at 3 PRs (Figure 8), the XPS analysis showed that at least 7 PRs were required to deliver virtually carbon-free TiO₂. High-resolution XPS C1s spectra showed that the residual carbon in the film is a mixture of C–H, C–O, and C=O bonds for the samples deposited with 1–5 PRs (Figure S2). N was present in the film likely due to a contribution of NₓOₓ species formed in the N₂/O₂ plasma. Nitrogen content decreased slightly by increasing the plasma exposure time. High-resolution N1s peak of TiO₂ layers deposited with 1 and 10 plasma PRs is shown in Figure 9. Both films showed three peaks at around 400, 402, and 407.5 eV. The peak around 400 eV is ascribed to molecularly adsorbed nitrogen such as NOₓ,[36–38] while the smaller peak at around 402 eV can be assigned to Ti–N–O bonds.[35] The peak at 407.5 eV is

**TABLE 3** Chemical composition (determined by XPS) of the ALD TiO₂ layers prepared with different number of print repeats and hence varying plasma exposure times

| PR in each ALD cycle | Total plasma pulse length (ms) | Atomic % [C] [N] |
|----------------------|-------------------------------|-----------------|
| 1                    | 0.4                           | 5.1 3.0         |
| 3                    | 1.2                           | 2.7 2.6         |
| 5                    | 2.0                           | 2.0 2.4         |
| 7                    | 2.8                           | <1.0 1.8        |
| 10                   | 4.0                           | <1.0 1.9        |

Note: The samples were deposited with 475 ms of TTIP exposure time and no extra purge time. The maximum error in measuring C and N by XPS is 0.5 at.%.

Abbreviations: ALD, atomic layer deposition; PR, print repeat; XPS, X-ray photoelectron spectroscopy

**FIGURE 8** Growth per cycle (GPC) of atomic layer deposition (ALD) layer as a function of the number of plasma repeats in each ALD cycle. The GPC is calculated from the thickness measured by ex situ spectroscopic ellipsometry after 100 ALD cycles on c-Si. The corresponding plasma exposure time is also given in the top horizontal axis. Data are given for 475 ms of TTIP exposure time and no extra purge time. No purge time was selected to avoid extremely long deposition times. PR, print repeat

**FIGURE 9** High-resolution (a) Ti2p and (b) N1s X-ray photoelectron spectroscopy spectra of the TiO₂ films prepared by two different number of N₂/O₂ plasma print repeats (PRs) in each atomic layer deposition cycle. The spectra were recorded before sputtering of the films with Ar ions
attributed to NO3 bonds. This peak only appeared in the surface XPS scans and was absent upon the first step of Ar+ sputtering. The intensity of the peak at 407.5 eV was much lower when the plasma exposure time was prolonged. Furthermore, Ti2p peaks of the films deposited by 1 and 10 plasma PRs (Figure 9a) are slightly shifted to lower binding energies, associated to N-bonded Ti atoms as observed in the previous section for CVD TiO2 films on glass.

In addition to XPS, we also carried out RBS/ERD analyses on two TiO2 films deposited at different plasma exposure times (Table 4). The RBS measurements did not show any carbon present in the films, suggesting that the latter was below the detection limit of the method (5 at.%). This is in line with the XPS results which showed 4.2 at.% and <1 at.% of C for samples deposited with 1 and 10 PR, respectively. Both RBS and XPS showed a decrease in N content by increasing the number of PRs in each ALD cycle. ERD measurement showed a decrease in hydrogen content by increasing the number of PRs. Larger contents of carbon and hydrogen in the film obtained with 1 PR suggest that CHx and OH species are present in the layer.

The refractive index of the TiO2 film increased from 1.86 to 1.98 by prolonging the plasma exposure time (Table 4), further indicating the role of plasma reactive species in controlling film properties. The plasma exposure time in this study was in the order of few milliseconds, which is considerably shorter than the plasma duration in most of the previous studies reported in the literature. The lowest plasma exposure time during a ALD process was reported by Poodt et al. for Al2O3 deposition by spatial ALD (100 ms). One of the key differences between our process and more standard ALD processes, besides the working pressure, is the geometry of the chamber. The plasma was generated in a small gap of 150 µm and the O radicals were created in proximity of the surface where the reactions take place. Therefore, we argue that reactions were possibly limited by the reaction rate rather than by transport rate of species to the surface.

The ALD process of TiO2 films using the microplasma printer showed its potential in delivering TiO2 films with low levels of impurities when compared to layers deposited under CVD mode. In the next section, we present the preliminary analysis of the spatial resolution which can be achieved by both deposition modes.

### 3.3 Spatial resolution of microplasma printed TiO2 layers

The printing resolution of the microplasma printer in CVD and ALD mode is addressed in this section. Note that the printing resolution is defined as the smallest feature that can be deposited by the microplasma printer. It is worth mentioning that the previous study using the same microplasma printer for surface functionalization using an organic molecule showed a submillimeter to millimeter-range resolution. To test the resolution for the case or inorganic material deposition, lines of TiO2 (10-mm long) were deposited on c-Si by using one needle electrode in CVD mode and two needle electrodes in ALD mode by the microplasma printer as discussed in the experimental section. XPS line scans were performed perpendicular to the lines to estimate the width of the deposited TiO2 lines. Figure 10a shows the elemental concentration perpendicular to the TiO2 line deposited in CVD mode with one needle electrode and 20 PR (53 sccm of TTIP without O2). The point where the Ti and Si signals started to increase and decrease, respectively, was defined as the edge of the pattern. As can be seen from the graph, Ti was also detected in areas outside the pattern, which can be related to diffusion of the gas phase species to the surrounding areas of the line. However, the area where the Ti signal was consistently higher than the surrounding regions was measured to be 2,000 µm (distance between the two dashed lines in Figure 10a). Since the deposition area was not sufficient to carry out spectroscopic ellipsometry measurements, we estimated the thickness from XPS analysis (details in the Supporting Information). The thickness of TiO2 layer was measured to be

### Table 4 ALD TiO2 film properties for two different number of PRs

| PR in each ALD cycle | Extra purge time (s) | Total plasma exposure time (ms) | Atomic % by XPS | Refractive index |
|----------------------|---------------------|---------------------------------|-----------------|-----------------|
| 1                    | 10                  | 0.4                             | 4.2             | 1.86            |
| 10                   | 10                  | 4.0                             | <1.0            | 1.98            |

Note: Relative error in number of Ti atoms deposited per cycle is 5% and for Ti: 2%, O: 4%, and N: 2% (these elements were all determined by RBS). H content is measured by ERD and the relative error is 10%. Detection limit of RBS for N and C is 2 and 5 at.% respectively. The errors in measuring N and C by XPS do not exceed 0.5 at.%. The refractive index n was derived from the spectroscopic ellipsometry data.

Abbreviations: ALD, atomic layer deposition; ERD, elastic recoil detection; PR, print repeat; RBS, Rutherford backscattering spectrometry; XPS, X-ray photoelectron spectroscopy
approximately 8 nm (±0.5 nm). The difference between the predicted thickness of 26 nm (according to the growth rate determined earlier by ellipsometry when all needles were used) and effectively deposited thickness can be explained by the difference in gas flow distribution when one needle or multiple needle electrodes are used. Furthermore, the thickness of the TiO₂ layer deposited on the vicinity areas of the line was estimated by XPS to be approximately 5 nm (±0.5 nm).

Figure 10b shows the XPS line scan of the TiO₂ line deposited by the microplasma printer in (a) chemical vapor deposition mode, 20 PR with one needle electrode and (b) atomic layer deposition mode with two needle electrodes, 50 ALD cycles and 1 PR in each cycle.

Figure 10b shows the XPS line scan of the TiO₂ line deposited by the microplasma printer in (a) chemical vapor deposition mode, 20 PR with one needle electrode and (b) atomic layer deposition mode with two needle electrodes, 50 ALD cycles and 1 PR in each cycle.

4 | CONCLUSION

Plasma-enhanced CVD and ALD processes were developed for area-selective deposition of TiO₂ films by employing an atmospheric pressure microplasma printer. The CVD process by the microplasma printer enabled deposition of TiO₂ with a growth rate of 1.3–2.3 nm per PR. The lowest C concentration in the CVD films was found equal to 5.0 ± 0.5% and the refractive index did not exceed the value of 1.8, even after adding O₂ to the gas mixture. In contrast, ALD, the microplasma printer, delivered virtually carbon-free TiO₂ films with a refractive index of 1.98 by increasing the N₂/O₂ plasma exposure time up to 4 ms. A GPC within the range of the reported values in the literature was obtained in ALD mode. Furthermore, the plasma measured by ellipsometry (GPC: 0.15 nm) was about 7.5 nm (±0.1 nm) and the estimated thickness from XPS measurements was about 7 nm (±0.5 nm) in the middle of the line when using two needles. The thickness of the TiO₂ at the areas outside the line in Figure 10b was estimated around 3 nm (±0.5 nm) by XPS. The film growth in the proximity of the patterned area is possibly due to diffusion of species produced in the N₂/O₂ plasma to outside the patterned area and reaction with the adsorbed precursor molecules on the surface. Moreover, the amount of carbon at areas outside the line was more than 40%. This carbon-rich TiO₂ may be formed due to incomplete reaction between TTIP and residual of plasma species, that is O radicals, O₃, and NₓOᵧ, diffused to the vicinity areas. Finally, to demonstrate the capability of the microplasma printer to print patterns under ALD mode, a simple “2”-shaped pattern was printed as shown in Figure 11 on c-Si aiming at a TiO₂ thickness of 30 nm.
exposure time in the ALD process was found to be a key parameter to control the properties of TiO$_2$ films. Separation of the TTIP and plasma exposures in ALD allowed using sufficiently long plasma exposure times in each ALD cycle, which could not be achieved in the CVD process. Preliminary tests were performed to estimate the printing resolution of the two techniques. Lines of TiO$_2$ were deposited by one or two needle electrodes, and it was shown that for the same film thickness, the resolution of the line deposited by ALD is better than the one deposited by CVD. Further research is required to improve the printing resolution of the patterns which can pave the way to potential applications of the plasma-printing technology in area-selective deposition of inorganic compounds.

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**SUPPORTING INFORMATION**

Additional supporting information may be found online in the Supporting Information section.

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