Photocatalytic activity of TiO$_2$ deposited by reactive HiPIMS with long target-to-substrate distance

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ABSTRACT

Reactive High Power Impulse Magnetron Sputtering (HiPIMS) of TiO$_2$ thin films was carried out to investigate the influence of ion parameters and the deposition temperature on the film crystallinity and photocatalytic performance. In order to limit unintentional substrate heating, a deposition setup with long target-to-substrate distance was used. Different HiPIMS pulse configurations, deposition temperatures and substrate bias were evaluated. TiO$_2$ films prepared by pulsed dc magnetron sputtering were used as reference. Films deposited at room temperature were all found to be X-ray amorphous, and a minimum temperature of 200 °C was needed for film crystallization irrespective of the mode of operation. This is attributed to the relatively long target-to-substrate distance of 180 mm used in this work. The growth of a specific polymorph was shown to be dependent on the operation mode, where a high oxygen partial pressure was ideal for anatase formation. The photodegradation rates were, as expected, found to be highest for crystalline samples, where single- and mixed-phase films yielded similar rates. Furthermore, the photodegradation rates of HiPIMS films deposited without substrate heating could be enhanced up to 3 times as compared to the corresponding pulsed dc reference film. The ion assistance in HiPIMS is also beneficial at moderate temperatures, here 200 °C, where an improved crystallinity as compared to pdcMS, was observed.

1. Introduction

TiO$_2$ is a versatile material with a multitude of applications including photocatalysis and water splitting [1]. Among the TiO$_2$ polymorphs, anatase has been reported to have the highest photocatalytic activity, and it is therefore desired for self-cleaning and antimicrobial surfaces as well as for air and water cleaning [2,3]. The photoactivity can be further increased by optimization of the exposed facets [4]. TiO$_2$ thin films are attractive in surface engineering, where they can combine their photocatalytic functionalities with advantageous mechanical and optical properties.

An important factor limiting the use of photocatalytic TiO$_2$ is the growth temperature required for synthesis of crystalline thin films. Even if anatase is the low temperature polymorph, temperatures in excess of 300 °C are required to achieve appreciable crystallinity by thermal annealing of amorphous thin films [5]. When temperature is employed during the deposition via substrate heating, anatase can be achieved at about 200 °C by reactive magnetron sputtering [6]. Reducing the temperature to enable TiO$_2$ deposition on temperature sensitive substrates, such as polymer foils, is an important research challenge.

For this reason, early reports on low temperature synthesis of crystalline TiO$_2$ by High Power Impulse Magnetron Sputtering (HiPIMS) [7] and high photocatalytic activity of such thin films [8] have attracted much attention. This is because HiPIMS, as a variant of magnetron sputtering, is a scalable industrially viable alternative to the traditional pulsed dc magnetron sputtering (pdcMS) deposition. In HiPIMS, a substantial fraction of the sputtered material is ionized thanks to a high instantaneous plasma density achieved in a sputtering discharge operated with low duty cycle and higher pulse power density [9]. Ionization of the sputtered flux enables more effective tuning of the energy of impinging species by e.g. a substrate bias. Film morphology and crystallinity can be significantly affected by the hyperthermal ions created in HiPIMS [10]. The combination of plasma activation and ion assistance offers an alternative to substrate heating and thus facilitate low

Abbreviations: HiPIMS, High Power Impulse Magnetron Sputtering; pdcMS, Pulsed-DC Magnetron Sputtering; RT, Room Temperature; OM, Oxide Mode; GIXRD, Grazing Incidence X-ray Diffraction.

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temperature growth [11]. This approach has been employed to densify the microstructure and tune the surface roughness of thin films [12], but also to be able to have a better control of crystalline grain growth [13].

Among published studies of HiPIMS synthesis of TiO\textsubscript{2} films, Konstantinidis et al. [7] showed that moderate peak power density and low ion energy (electrically floating substrates) resulted in anatase growth while high-energy ion bombardment led to formation of rutile. The effect of peak power density has been confirmed by Amin et al. who also highlighted the role of energetic negative O\textsuperscript{−} ions [14]. Cemin et al. systematically studied the impact of external process parameters including the substrate temperature and deposition pressure [13]. In general, there is a correlation between the energy of impinging species and the dominant crystal phase [15]. The studies above, however, mention substrate heating during the deposition. For instance, Amin gives “less than 170 °C” while Mraz 70–140 °C and Musil [6] 100–150 °C depending on the discharge power.

This work aims to investigate the relation between growth conditions and photocatalytic activity of TiO\textsubscript{2} in a configuration where a longer distance limits unintentional substrate heating, thus disentangling ion flux parameters from substrate heating effects. Different HiPIMS pulse configurations were explored to address the influence of ion parameters in the process, using a pdcMS process for comparison purposes. Deposition temperature, substrate bias, as well as the mode of operation in the reactive process were also studied to understand the impact of different deposition conditions. The photocatalytic efficiency was assessed by quantifying the photo-degradation of stearic acid (SA). Unlike dye degradation tests, where the sample is fully submerged in a solution containing a concentration of a specific dye with specific redox properties (that sometimes reversibly go back to the initial state after photon illumination), the chosen photocatalytic characterization method relies on the decomposition of a stearic acid layer deposited on top of the film. It does not have any concentration dependent variables and is independent of the film’s topography.

2. Experimental section

TiO\textsubscript{2} films were deposited by reactive magnetron sputtering in a deposition system CMS-18 (Kurt J. Lesker), illustrated in Fig. 1. The system consists of a cylindrical process chamber with a volume of about 75 L pumped by a cryopump (CTI CryoTorr 8) to a base pressure of about 5 × 10\textsuperscript{−}5 Pa or better, and a load-lock. It is equipped with four magnetron sputtering sources in a co-sputtering configuration with the target-to-substrate distance of 180 mm. A single Ti sputtering target (99.99 % purity) with a diameter of 100 mm and thickness of 6 mm was used here and operated either in pDCMS or HiPIMS mode. Ar and O\textsubscript{2} with purity of 99.9995 % were supplied by means of mass flow controllers with the Ar mass flow kept constant at 60 sccm. All depositions were carried out at a constant total pressure of 0.8 Pa maintained by means of a downstream pressure controller.

Separate gas inlets for Ar and O\textsubscript{2} were used, where the Ar was admitted to the sputtering source equipped with a short chimney and the O\textsubscript{2} introduced via a distribution ring around the substrate holder. This way, a gradient in the O\textsubscript{2} partial pressure may be achieved that delays the transition from the metal to oxide mode of reactive sputtering. Thus, stoichiometric TiO\textsubscript{2} could be achieved at a relatively high deposition rate in the metal mode of operation [12]. However, careful tuning of the oxygen mass flow is required to prevent the process from transitioning to the oxide mode. Upon analyzing the hysteresis loops, the specific operation points in the metal mode were chosen by increasing the oxygen flow as much as possible, while still keeping the process stable during the whole run. Oxide mode films were grown with an oxygen flow slightly higher than the transition threshold. The discharge power was provided either by a pulsed DC power supply Pinnacle+ operated at a frequency of 50 kHz and reverse time of 1.6 μs, or by a Hipster 1 HiPIMS power supply. Different pulse configurations were used for the HiPIMS experiments as summarized in Table 1. In all cases, the average discharge power was maintained at 500 W. To further inspect the impact of the ion energy on the film microstructure, two values of the substrate bias were applied for selected conditions in addition to depositions without bias. Pulsed substrate bias was used with the pulses synchronized with the discharge pulses and the on-time 100 μs longer. When no bias was used, the substrate was kept grounded.

Si substrates were placed on a rotating substrate holder equipped with a radiative back-side heater. All conditions were explored either without intentional heating (nominal room temperature, RT) or heated between 100 and 400 °C. In order to ensure reproducible deposition conditions, each deposition started with pre-sputtering of the target in pure Ar, then O\textsubscript{2} was introduced into the deposition atmosphere, while still protecting the substrate from deposition by means of a shutter.

The deposition rates were determined from the thicknesses of test films measured by a Veeco Dektak 150 stylus profilometer and the respective deposition times. The sample thicknesses were kept in the range of 100 to 200 nm to ensure all film properties are comparable.

The coating morphology was evaluated by SEM using a Zeiss Merlin overview of the deposition conditions used for TiO\textsubscript{2} growth, based on employed sputtering energy sources and operation modes. “RT” stands for room temperature.

<table>
<thead>
<tr>
<th>Sputtering method</th>
<th>Deposition parameters</th>
<th>Duty cycle (%)</th>
<th>Substrate temperature (°C)</th>
<th>Reactive mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>HiPIMS</td>
<td>( f = 200 \text{ Hz} ) ( \tau_{\text{ON}} = 50 \mu s )</td>
<td>1</td>
<td>RT, 200, 400</td>
<td>Metal mode</td>
</tr>
<tr>
<td></td>
<td>( f = 1 \text{ kHz} ) ( \tau_{\text{ON}} = 50 \mu s )</td>
<td>5</td>
<td>RT</td>
<td>Metal &amp; oxide modes</td>
</tr>
<tr>
<td></td>
<td>( f = 1 \text{ kHz} ) ( \tau_{\text{ON}} = 100 \mu s )</td>
<td>10</td>
<td>RT, 200, 400</td>
<td>Metal &amp; oxide modes</td>
</tr>
<tr>
<td>Pulsed dCMB</td>
<td>( f = 50 \text{ kHz} ) ( \tau_{\text{ON}} = 18.4 \mu s )</td>
<td>92</td>
<td>RT, 200, 400</td>
<td>Metal &amp; oxide modes</td>
</tr>
</tbody>
</table>

\( f \) — pulsing frequency, \( \tau_{\text{ON}} \) — pulse on-time.
In order to evaluate the photocatalytic activity, stearic acid decomposition was investigated as described elsewhere [17,18]. Degradation of the acid spin-coated on the test surface was monitored by in-situ FTIR (Fourier-transform infrared spectroscopy) under 365 nm UV illumination with an irradiance of 1.2 mW/cm² [11]. The stearic acid concentration on the surface was evaluated from the absorbance spectrum and fitted by a pseudo zero-order reaction kinetics [19] as:

\[ C(t) = -k_d t + C_0 \]  

where \( C \) is the stearic acid concentration (molecules-cm\(^{-2}\)) and \( C_0 \) is the initial stearic acid concentration. \( k_d \) is the degradation rate constant (molecules-min\(^{-1}\)-cm\(^{-2}\)), the observed reaction rate. The total measurement time, \( t \), was 120 min in this work. With the concentration proportional to the area of characteristic SA absorbance peaks \( A(t) \), the apparent reaction rate \( k_{app} \) in units of min\(^{-1}\) was extracted from the slope of the linear fit as follows:

\[ \frac{A_{100} - A_0}{A_0} = k_{app} \]  

The reaction rate \( k_{app} \) was determined from the first 20 min of irradiation. This way, the attained rates are not influenced by the reaction by-products. However, for samples with lower reaction rates, the fraction of decomposed stearic acid was determined after 100 min of photo-degradation. This extra parameter provides additional differentiating information about the samples’ performance and allows a more accurate distinction between the less photoactive surfaces. An example of the different photocatalytic performances over time can be seen in Fig. SI.1. By taking the absorbance peaks’ area from the first and 100th min, such could be calculated by:

\[ [SA] = 1 - \frac{A_{100}}{A_0} \]  

3. Results and discussion

This section is organized as follows: first, the deposition process was characterized in order to determine suitable deposition points for each mode of operation. Then, the microstructure of films was analyzed by X-ray diffraction and SEM, and the effect of different process parameters is discussed. Finally, the photocatalytic activity was determined for a set of selected samples and the results are related to the growth conditions.

3.1. Deposition process characterization

Initially, the deposition processes were characterized with respect to the oxygen flow. The process curves for deposition rate and discharge voltage are shown in Fig. 2 for the reference pdcMS and all studied HiPIMS pulse configurations. The highest deposition rate was observed for pdcMS, while HiPIMS displayed considerably lower values. The deposition rate in HiPIMS also decreases with decreasing duty cycle. This effect is well known and is attributed to the combination of metal ion back-attraction, that leads to self-sputtering and reduced ion flux to the substrate, and the non-linear evolution of the sputtering yield with the incident ion energy given by the discharge voltage [4,5]. Indeed, as the peak power density increases with decreasing duty cycle, a progressively larger fraction of the sputtered atoms becomes ionized and may be attracted back to the target, replacing sputtering by Ar ions with self-sputtering by the ionized metal. The waveforms for 10 % and 1 % duty cycles in both reactive modes of operation can be seen in Fig. SI.2. In the case of a highly ionized sputtered flux, 70–90 % of the metal ion population has been reported to be attracted back towards the target [20]. Additionally, for depositions with identical average power, the discharge voltage for HiPIMS is generally higher compared to pdcMS, as illustrated in Fig. 2b. However, due to the non-linear dependency of the sputtering yield \( Y \) on the discharge voltage \( V_D \) as \( Y \sim \sqrt{V_D} \), the sputtering yield increase does not fully compensate the lower discharge current and therefore the deposition rate is reduced [21–23].

In all the studied cases, a clear hysteresis loop can be observed. The transitions between the so-called metal mode of deposition (MM), where the sputtering target surface is predominantly metallic, and the poisoned...
or oxide mode (OM), with the target surface covered by a layer of compound oxide material, are caused by the reaction of reactive gas molecules with target metal atoms [24]. The width of the hysteresis loop is affected by the used HiPIMS conditions. A progressive reduction of the hysteresis width with decreasing duty cycle is visible for the HiPIMS processes and is caused by a lower overall deposition rate as compared to pulsed DC with a corresponding reduction of the oxygen flow, and also the reactive gas rarefaction close to the target surface [24]. The phenomenon was already reported for HiPIMS processes, also leading to gradual, hysteresis-free transitions to the compound mode [25,26].

Curves concerning the lowest duty cycle of 1 % are shown only for the MM. Here, the measured peak current densities after the transition to the OM were extremely high in comparison with 10 % duty cycle and the operation was not stable.

The investigated deposition conditions are expected to have pronounced impact on the film’s microstructure and, consequently, on its properties, including the photocatalytic performance. The operating modes (metal/oxide) differ significantly. In the MM, relatively high density of metal species is expected, due to the high metal sputtering yields as exemplified by high deposition rates. Upon target oxidation, the process transitions to the poisoned state. Here, the metal sputtering rate drops dramatically. As a result of the higher metal atom density in the MM plasma, reduced electron temperature is expected due to the lower first ionization energies of Ti (6.8 eV compared to 15.75 eV for Ar). In contrast, in the OM, the electron temperature is determined mainly by the Ar that sustains the discharge current [27,28]. Higher ionized metal flux fraction is therefore expected in the OM for the same duty cycle.

3.2. Film crystallinity

Film crystallinity was evaluated primarily by means of GIXRD and complemented by 0–20 measurements and crystallite size calculations. The average crystallite dimensions were obtained for the most common and intense reflections of each phase, anatase (101), rutile (110) and (101).

The deposition temperature is the most important factor influencing the crystallization. In the MM, rutile is the dominating crystal phase in samples deposited with substrate heating as seen in Fig. 3. Diffraction peaks start to appear at 200 °C for HiPIMS films. However, the peaks are rather broad, indicative of small crystallite sizes. pdcMS films are X-ray amorphous at this temperature. At 400 °C, the diffractograms alter considerably for both deposition methods. Now, the pdcMS films have higher peak intensities compared with the HiPIMS films. This result agrees with those reported by Agnarsson et al. [29] carried out at 600 °C.

Fig. 4 shows corresponding XRD results for films deposited in the OM. Anatase films can be achieved at 200 °C. The peaks are considerably sharper than in the MM at the same temperature, indicative of greater crystallite sizes. There was no rutile detected in any of the OM films. While pdcMS coatings only show diffraction from the most common anatase plane (101), HiPIMS registered not only a more intense reflection for the same plane, but also revealed diffraction peaks at higher 20 values. A further increase of the deposition temperature has a negligible effect on the HiPIMS films crystallinity.

Among the HiPIMS MM set, there are still significant differences in terms of crystallinity when the duty cycle is considered. In the case of the 10 % duty cycle, traces of anatase (101) were also identified in samples grown at 400 °C, in contrast to films made by pdcMS. Increasing the ionized flux fraction at 1 % duty cycle did not improve the crystallinity. This can be clearly seen from the rutile (101) peak in Fig. 3. However, at 200 °C, small amounts of rutile are seen in the HiPIMS film deposited with 1 % duty cycle without substrate bias, in contrast with the 10 % films.

No crystalline TiO₂ was achieved without substrate heating irrespective of the deposition conditions. Increasing the ionized flux fraction by reducing duty cycle did not show any tendency for crystallization according to XRD. Neither had the ion energy controlled by the use of substrate bias. For the heated depositions, small changes related to the substrate bias can be observed in the MM. In the OM, the substrate bias does not affect the crystallinity. Nonetheless, as discussed in the next section, the substrate bias can be used to tune the film microstructure.

Furthermore, 0–20 scans (not shown) did not reveal any preferential orientation. As for the calculated grain sizes, displayed in Table SI.1, no significant trend was seen. The sizes were comparable in both reactive modes in spite of the MM films being thicker than the OM. In the OM, the film deposited at 400 °C exhibited larger average crystallite size compared to the one grown at 200 °C, which is expected owing to the larger diffusion lengths of as-deposited particles at the higher temperature.

Considering the chamber geometry, the high substrate-to-target distance may be one of the main differences from previous studies that report low temperature-growth of crystalline TiO₂ [7,13–15]. A short distance between the cathode and the substrate leads to unintentional heating of the substrate caused by the discharge plasma. The role of substrate temperature was explored by depositing at 100 °C in both MM and OM, using the same deposition conditions without substrate bias. However, no crystallinity was achieved in any of the coatings (not shown). As shown in Fig. 4, HiPIMS is beneficial for the formation of anatase at the intermediate temperature of 200 °C, where an improvement over the pdcMS is observed. OM deposition, with high partial pressure of oxygen and low deposition rate is necessary to achieve crystallinity, in agreement with findings of Musil et al. [30].

3.3. Microstructure

Cross-sections of the thin films were inspected by SEM. The majority of films exhibited a typical columnar microstructure. Generally, TiO₂
films deposited at RT by magnetron sputtering are X-ray amorphous and columnar, possibly with nanosized crystals [32]. Such results are not surprising given the associated low temperature, where the short diffusion length of deposited particles leads to the columnar microstructure as well as lack of crystallinity [29].

As it can be seen in Fig. 5, the use of substrate bias changed significantly the microstructure of films provided that sufficient metal ionization was achieved. The columnar microstructure is replaced by a dense and feature-less morphology. This is a result of the densification caused by energetic ions. The OM 10% duty cycle was the most affected when bias was applied due to the large metallic ion population. MM employing 10% duty cycle on the other hand, shows negligible difference both in film densification and surface smoothening when bias is applied, in agreement with the expected low ionized metal flux fraction mentioned earlier. As pdcMS plasmas allow for very little ionization, the bias also has no effect in the same way as seen for higher duty cycle HiPIMS. Sufficient ionization gives hence the possibility to tune the film microstructure by the substrate bias according to the specific application [33].

The effect of temperature is illustrated in Fig. 6. The figure compares films deposited at room temperature with those deposited at 400°C. As expected, noticeable changes are seen. In the MM, both films show well-developed crystallites at 400°C, which are more evident at higher duty cycle, which agrees with the better crystallinity shown in Fig. 3. For the OM film, the heating induces similar changes as in the MM with column widening and changed surface topography. It is well-known that enhanced surface diffusion promotes the growth of crystals.

### 3.4. Photoactivity

The photoactivity of the deposited films was evaluated by the decomposition of stearic acid. The apparent reaction rates, \( k_{app} \), were determined from zero order reaction kinetics (Eq. 1), according to Eq. (2), and are shown in Fig. 7a). The reaction rates were determined from the initial 20 min. For films with low reaction rates (i.e. grown at room temperature), the amount of decomposed stearic acid was determined from the surface concentrations after 100 min irradiation, Fig. 7b).

As expected, the deposition temperature is the primary parameter affecting the performance. The highest temperature yields the most active films, irrespective of the deposition method, and such is connected to the crystallinity observed by the GIXRD measurements. For films deposited without any heating, considerably lower rates are seen, as expected from the X-ray amorphous structure. The role of crystallinity on the photocatalytic properties of TiO\(_2\) is well known [34]. Anatase is the desired phase, in particular the (001) facet is reported to exhibit high photocatalytic activity for some oxidation reactions. The impact of this particular phase in photoactive TiO\(_2\) films deposited in the MM and OM can be demonstrated by Fig. 7a). Comparable performance is seen for OM films deposited at 200°C, with the anatase phase, and MM at 400°C, that shows a rutile or mixed phase. When the OM film is grown at 400°C, the reaction rate is almost twice of the MM deposited at the same temperature. The increase in the registered rates of heated depositions in the OM could be related with a larger grain size (Table SI). One of the main reasons for the similar photoactivity observed for OM films at 200°C and MM films at 400°C is most likely related with the phase composition of the films. As described in Section 3.2, lower oxygen
partial pressure in the MM results in the mixed phase films, whereas higher partial pressure (i.e. OM) yields an anatase dominated film. However, mixed phase anatase-rutile materials, such as the commercial P25 from Degussa, are also reported to have beneficial inter-crystal properties [35]. Interestingly, the most active film in this study is a rutile TiO$_2$ film deposited by pdcMS in the MM at 400 °C. Its GIXRD spectrum shows a clearly better crystallized lattice than any HiPIMS with 10 % duty cycle. These results open up a possibility of high deposition rates that are achievable in the MM, while still preserving the photocatalytic attributes. However, more detailed characterization of the thin film is required to draw further conclusions. Given that our main focus are the RT depositions, no further analysis of the high temperature films was carried out. Rather, they serve as a basis for comparison with the RT films.

The RT coatings exhibit lower activities as expected from X-ray amorphous TiO$_2$. There are, however, clear differences in their reaction rates depending on the growth conditions. Given the relatively high noise of the FTIR measurements, the fraction of decomposed SA after 100 min is analyzed in Fig. 7b). Obviously, the HiPIMS coatings are generally more active than the ones prepared by pdcMS, independent of the mode of operation. At a high deposition rate and low oxygen partial pressure, in the MM, low peak power has a positive effect on the photocatalytic performance, as seen for the film prepared using 10 % duty cycle. The 10 % HiPIMS coatings registered more than 3 times the

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**Fig. 6.** Influence of substrate temperature on TiO$_2$ films deposited by HiPIMS without substrate bias, where the left and right column refer to depositions at room temperature and 400 °C, respectively. Micrograph legends show the sputtering mode of operation, pulsing duty cycle and deposition temperature, successively.

**Fig. 7.** a) Zero-order apparent reaction rate for decomposition of stearic acid under UV irradiation, $k_{app}$ over a period of 20 min. The film data is arranged according to the sputtering method, HiPIMS or pdcMS, followed by the deposition temperature. Data labels refer to the corresponding reaction rates and crystalline phases, while different symbols relate to the use of substrate bias, as seen in the legend. b) Decomposed fraction of stearic acid for room temperature films, after 100 min of UV irradiation, determined according to Eq. (3). Both figures’ x-axis labels describe the sputtering operation mode, pulse duty cycle and substrate bias voltage, respectively.
reaction rate compared to the 1 % and even higher than MM pdcMS. Relatively limited metal ionization is expected for 10 % as compared to the 1 % duty cycle as discussed earlier. Apparently, excessive ion bombardment in the case of 1 % MM, has detrimental effect in this specific application. On the other hand, in the OM HiPIMS, the higher metal flux ionization combined with the higher oxygen partial pressure is beneficial with respect to the SA decomposition. This specific sample was the most effective of all films deposited without substrate heating. The best photocatalytic performance for RT pdcMS coatings was also observed for the OM samples, confirming earlier reports by Kelly et al. and Marcelino et al. [36,37]. Similar trends are seen in the crystallized samples with respect to the mode of operation, except for the MM pdcMS grown at 400 °C. Nonetheless, the plasma conditions influence the grown films with respect to their microstructures and also photocatalytic properties, even when the matrices are X-ray amorphous. Tentatively, the presence of small crystallites in the films, invisible in the X-ray diffractograms, could be linked to the different photocatalytic performances seen.

The impact of substrate bias in RT films was also analyzed. Increasing the particle energy is obviously detrimental as shown from the reaction rates and decomposed SA content in OM RT samples. The films prepared using 10 % duty cycle HiPIMS in the OM without substrate bias performed better in all cases. A tentative explanation could be the pronounced film densification seen for this particular example in Fig. 5. As a result of the highly ionized sputtered flux and intense bias voltage, the ion impact energy upon deposition will disturb the forming film. Computer simulations predict that excessive ion energy suppresses the growth of anatase [7,14].

4. Conclusions

Our results highlight the complexity of the reactive HiPIMS deposition process. With the relatively long target-to-substrate distance of 180 mm used in this work, we conclude that ions produced in HiPIMS, employed a wide range of parameters, do not seem to be sufficient for the crystallization of TiO2. Interestingly, crystalline films were not achieved at a temperature of 100 °C either. However, the photoactivity of the films deposited at room temperature is still enhanced by the use of HiPIMS. HiPIMS is also beneficial at moderate temperatures, 200 °C in this study, where it improves the film crystallinity as compared to pdcMS deposited at the same temperature. One mechanism that requires further investigation is the plasma activation of O2 and its effect on the crystallization of TiO2 [7]. Additional O2 activation investigated by Stranak et al. [38] showed a positive impact on the formation of anatase in HiPIMS. The effect may be more pronounced for short deposition distances when, however, it may overall with the unintentional substrate heating.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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