Insight in the mechanisms responsible for anatase thin film growth in low pressure O_2/TTiP plasmas

W. Ravisy[1], A. Granier[1], M. Richard-Plouet[1], A. Goullet[1], B. Dey[2], S. Bulou[2], P. Choquet[2]

[1] *Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel, IMN, F-44000 Nantes, France*

[2] *LIST, Luxembourg Institute of Science and Technology, Belvaux, Luxembourg*

Abstract: This study concerns the growth mechanisms of photocatalytic TiO_2 anatase thin films deposited in a low pressure O_2/TTiP inductively coupled rf plasma. It focuses on the effect of the rf power and the TTiP fraction on the plasma composition and film structure in order to get deeper insight in the mechanisms and/or active species responsible for the anatase formation and growth.

Keywords: TiO_2, anatase, PECVD, O atoms, ellipsometry

1. Introduction

TiO_2 thin films have been extensively investigated in the literature for their photocatalytic and self-cleaning properties [1]. It has been shown that the TiO_2 anatase phase exhibit a much higher photocatalytic activity than the rutile phase. TiO_2 thin films and nanostructured TiO_2 have been deposited by various deposition processes such as sol-gel, magnetron sputtering, plasma enhanced chemical vapor deposition (PECVD) [2]. This latter is known for its ability to prepare amorphous or polycrystalline films at low temperature and to tune the film composition and optical properties.
In particular, it was previously shown that columnar polycrystalline anatase films can be prepared by PECVD at substrate temperature less than 120°C on Si and polymeric substrates [3] using a low pressure (4.0 10^{-3} mbar) rf inductively coupled plasma (ICP) from titanium tetra-isopropoxide (TTiP-$Ti(OC_3H_7)_4$) mixed with oxygen.

The anatase TiO_2 films deposited in an oxygen rich O_2/TTiP 98:2 ICP plasma at a rf power of 400 W were studied in detail. To investigate the anatase growth mode, the film growth was studied by real time in situ spectroscopic ellipsometry (RTSE) and the film morphology was investigated (ex situ after deposition) by Scanning Electron Microscopy (SEM) and transmission electron spectroscopy (TEM) for different film thicknesses. The coalescence of large polycrystalline columns emerging from an assembly of thin columns was found to happen at a critical thickness, designed as coalescence thickness hereafter. It was shown that this latter can be determined from RTSE analysis: it corresponds to a slope change in the variation of the film roughness as a function of the film thickness (as measured by RTSE). The coalescence thickness was measured to be about 150 nm in the oxygen rich O_2/TTiP 98:2 ICP plasma at a rf power of 400 W. In addition, the formation of large columnar structure was shown to be associated with an important increase in the photocatalytic activity. [4]

The aim of this study is to investigate the effect of the rf power and the TTiP fraction in the O_2/TTiP mixture both on the plasma composition and film structure in order to get deeper insight in the mechanisms and/or active species driving the anatase formation and growth.

2. Experimental conditions

The plasma was created in an oxygen rich O_2/TTIP mixture at a pressure of 4.0 10^{-3} mbar. The oxygen flow rate was fixed at 24 sccm and the substrate was at the floating potential. Further detail on the deposition reactor can be found in reference [3].
In this study, the rf power was varied in the 200-600 W range for a TTiP flow rate fixed at 0.24 sccm and the TTiP flow rate was varied from 0.07 to 0.7 sccm at a rf power of 400W. The different TTiP flow rate conditions are denoted as follows: A: 0.07 sccm, B: 0.10 sccm; C: 0.18 sccm, D: 0.24 sccm, E: 0.42 sccm and F: 0.7 sccm. Hereafter any deposited film will be denoted by the rf power followed by the letter corresponding to the TTiP flow rate, e.g. 400-D corresponds to a film deposited at 400 W with a TTiP flow rate of 0.24 sccm. The deposition time was tuned in order to deposit 250 nm thick films for all the conditions.

The plasma was analysed by optical emission spectroscopy. On the one hand, the emission intensities of CO, OH, H and Ar were measured at 297.7, 306.4, 486.1 and 419.8 nm, respectively and, on the other hand, the intensities of O and Ar lines were measured at 844 nm and 750 nm, respectively. In order to get partially free of the electron density and electron temperature variations upon power or TTiP flow rate variations, the intensities of CO, OH and H were divided by the intensity of the Ar line at 419.8 nm and the one of O by the intensity of the Ar line at 750 nm.

The film growth was monitored by RTSE which allows to determine the optical parameters (refractive index and optical band gap of TiO_2) and the coalescence thickness, as described in the introduction and in [4]. The structure and chemical composition of TiO_2 films deposited on silicon were investigated by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. Their morphology was analysed by scanning electron microscopy (SEM). Some films (deposited on polymeric substrates) were characterized by transmission

electron microscopy (TEM) after preparation by ultramicrotomy.
The photocatalytic properties were investigated by following the degradation of stearic acid (SA) by infrared absorption on the samples under UV light. The Formal Quantum Efficiency (FQE) was calculated as the number of SA molecules photodegraded by the incident photons, as described in detail in [5].

3. Results

Deposition rate

The deposition rate, as measured by ellipsometry, is shown to be almost proportional to the TTiP flow rate for the films deposited at 400 W (increasing from 0.4 to 4 nm/min) and to slightly decrease with the rf power for the films deposited at fixed TTiP flow rate (from 1.7 to 1.3 nm/min). As expected, the deposition in oxygen-rich O_2/TTiP mixtures is governed by the amount of TTiP injected and is thus proportional to the TTiP flow rate. The weak decrease of the deposition rate observed as the power is increased from 200 to 600 W, is more difficult to explain. It may be due to the fact that above 200W the power is high enough to efficiently break the TTiP (the plasma is created in the inductive mode in this rf power range) and that the film density slightly increases with the rf power (and the associated increase in the ion flux at the surface of the growing film).

Coalescence thickness

The coalescence thickness, as defined in the introduction section was determined (from RTSE measurements) for all the films. It appears to decrease as the power increases and the deposition rate decreases, which means that the higher the energy flux, the thinner the coalescence thickness. It was measured to increase from about 50 nm for 400-A to 300 nm for 200-D and 400-F. In addition, the coalescence thickness was shown to be a function of the Yasuda factor (defined as the power to deposition rate ratio), whether the power or TTiP flow rate was varied.

Plasma analysis

The variations of the intensities of CO, OH and H emissions divided by the Ar line as a function of the rf power and the TTiP flow rate are expected to be representative of the variations of CO, OH and H density. They are shown to increase almost linearly with the TTiP flow rate, which is consistent with the linear increase of the deposition rate as far as the density of TTiP fragmentation and/or oxidation by-products formed in the plasma are expected to be proportional to the deposition rate. On the other hand, they increase with the rf power, which is more difficult to interpret as far as the deposition rate was shown to slightly decrease with the rf power.

In addition, an absolute value of O atom density could be estimated from the 844 nm oxygen to 750 nm Ar line intensity ratio, using the procedure described in [6] (the creation of O by electron dissociative oxidation of O_2 and direct excitation of O are both taken into account in order to estimate the O atom density). It increases with the rf power and slightly decreases with the TTiP flow rate (deposition rate).

Film structure

XRD and Raman analyses indicate the presence of anatase in the films for all the deposition conditions investigated. Nevertheless, XRD patterns also show the presence of rutile (in addition to anatase) in the films 400-A and 400-B deposited at very low TTiP flow rates (e.g. with very low deposition rate and high value of the Yasuda factor).

Surface morphology

The surface morphology, anlyzed by SEM, shows bright sharp grains which correspond to large polycrystalline columns protruding at the surface. The surface density and average projected area of polycrystalline columns have been measured with the ImageJ software for all the samples. A typical SEM micrograph of the surface is displayed in figure 1.

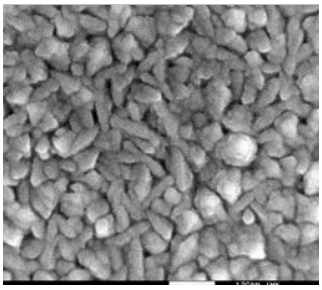

Fig. 1. SEM micrograph of the surface of the 400-C film (400W, 0.18 sccm TTIP flow rate). The white scale bar corresponds to 100 nm.

The density of polycrystalline grains is shown to increase, almost linearly with the rf power and to slightly decrease with the TTiP flow rate.

Photocatalytic properties

The FQE of the anatase TiO_2 films increases with the rf power, which is consistent with the increase of the density of polycristalline grains. As the TTiP flow rate is increased, the film structure was shown to vary with the presence of rutile for low TTiP flow rates (e.g. low deposition rate and high value of the Yasuda factor). The FQE of the films containing rutile (400-A and 400-B) appears to be much less that for the anatase TiO_2 films. The maximum value of the FQE is obtained for the films 400-C and 400-D which exhibit the highest density of polycrystalline grains.

Discussion

The density of polycrystalline grains on the sample surface is plotted as a function of the atomic oxygen density in figure 2 for the films deposited at different rf power and different TTiP flow rates. The density of polycrystalline grains at the surface appears to be proportional to the O atom density (in the plasma), whatever the deposition conditions (rf power or TTiP flow rate variations).

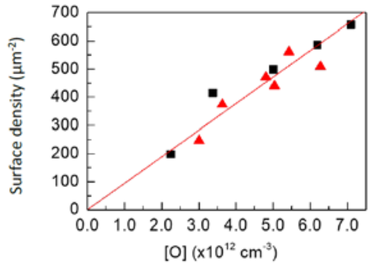

Fig. 2. Density of polycrystalline grains on the surface as a function of the atomic oxygen density: black squares: power series; red triangle: TTiP flow rate series

Hence it appears that O atoms have a key role for the formation of anatase seeds. When impinging on the growing film surface, O atoms recombine. The recombination energy is the main contribution to the energy flux transferred to the surface. It can be shown that in these plasma conditions, the energy transferred by the ions is much smaller than the energy transferred by O atom recombination. When plotting the density of polycrystalline grains as a function of the energy flux at the surface, a similar unique curve is obtained.

4. Conclusion

The growth of photocatalytic TiO_2 anatase thin films deposited in a low pressure O_2/TTiP inductively coupled rf plasma has been studied as a function of the rf power and the TTiP fraction. From the film and plasma analyses it is shown that O atoms have a key role for the formation of anatase seeds, as far as they are responsible of most of the energy flux at the surface of the growing film via their recombination. Hence, optimizing O atom density in a low pressure O_2/TTiP plasma very likely allows to favour the anatase formation.

5. Acknowledgements

The authors gratefully acknowledge the financial support of the French Agence Nationale de la Recherche (ANR) and Luxembourgish Fonds National de la Recherche (FNR) through the FNR-ANR-INTER project PATIO (ANR-17-CE08-0045-01 and INTER/ANR/16/11565003/ PATIO/Choquet).

6. References

[1] L. Sirghi, Plasma Sources Sci. Technol. 25 033003 (2016)
[2] M. Nasr, C. Eid, R. Habchi, P. Miele and M. Bechelany, ChemSusChem, 11, 1-26 (2018)
[3] D. Li, N. Gautier, B. Dey, S. Bulou, M. Richard-Plouet, W. Ravisy, Appl Surf Sci. 491:116–22 (2019)
[4] W. Ravisy, M. Richard-Plouet, B. Dey, S. Bulou, P. Choquet, A. Granier, A. Goullet, J. Phys. D : Appl. Phys 55 505303 (2022)
[5] A. Mills, J. Wang, J. Photochem. Photobiol. A: Chem.182:181–186 (2006)
[6] A. Granier, G. Borvon, A. Bousquet, A. Goullet, C. Leteinturier, A. van der Lee, Plasma Processes and Polymers 3, 365-373 (2006)