This is an author-deposited version published in: http://oatao.univ-toulouse.fr/
Eprints ID: 3978

To link to this article:
DOI:10.4028/www.scientific.net/KEM.415.1
URL: http://dx.doi.org/10.4028/www.scientific.net/KEM.415.1

To cite this version: Maury, Francis and MUNGKALASIRI, J. (2009) *Chemical Vapor Deposition of TiO2 for Photocatalytic Applications and Biocidal surfaces.* Key Engineering Materials, vol. 415. pp. 1-4. ISSN 1662-9795

Chemical Vapor Deposition of TiO_2 for Photocatalytic Applications and Biocidal surfaces

F. MAURY[a] and J. MUNGKALASIRI[b]

CIRIMAT, CNRS/INPT/UPS, ENSIACET, 118 Route de Narbonne,
31077 Toulouse cedex 4, France

[a] francis.maury@ensiacet.fr, [b] jitti.mungkalasiri@gmail.com

Keywords: MOCVD; AACVD, DLICVD; TiO_2; Photocatalysis; Antibacterial surfaces;

Abstract. Through a few examples, we present a short review on properties and applications of TiO_2 films deposited by various CVD processes. The constraints due to the growth process make difficult optimization of properties that were correlated with microstructures. We focus on the photocatalytic activity in the visible range and on the antibacterial behavior of these functional thin layers.

Introduction

The materials and processes have to play a major role in the sustainable growth. New products and their applications will find economical developments only if they meet societal requirements. Concepts as *life cycle* and new rules as *REACH* and *sustainable assessment of technologies* have to be considered. As a result, there is an increasing effort for instance to find alternatives to replace some heavy metals, to synthesize advanced (nano-)materials for novel devices or to provide new functionalities to base materials by surface treatment or thin film deposition.

In this context some materials are very promising because they find applications in major areas such as energy, environment and health. Titania in the form of anatase is one of them. It can be used as nanometric powder or as functional thin film on a substrate. TiO_2 is attractive owing to its good chemical stability, biocompatibility [1] and remarkable electrical and optical properties. It is self-regenerating and recyclable. As thin film, it is candidate for optical (transparency, antireflective) and microelectronic (insulator, capacitor, gas sensors) devices as well as protective coating [2]. It is well known as photo-active material, *e.g.* in photovoltaic cells or as photocatalyst, and it is used to produce self-cleaning and antibacterial surfaces.

Essentially through results recently published by our group, we present a brief review of some key points which, once overcome, should increase the development of TiO_2 thin films.

Results and discussion

TiO_2 on steel: continuous CVD process. As for the glass industry, functionalization of steel sheet by nanometric thick layers will lead to new products for building industry, automotive, appliance… Anatase can be deposited by many processes but they must have a high deposition rate and be adaptable as scrolling process. Atmospheric pressure CVD using titanium tetra-*iso*-propoxide (TTIP) as molecular precursor is a suitable technique [3-5]. Table 1 show that growth rate as high as 1000 nm/min as been obtained. Aerosol assisted chemical vapor deposition (AA-CVD or pyrosol) allows a greater growth rate if TTIP is used without any solvent [6].

One of the advantages of CVD processes is the possibility to control a great variety of microstructures that obviously influences the properties. Fig. 1 shows various morphologies obtained with the CVD processes described in the caption: granular, dense, nanocrystalline, cauliflower-like, columnar. Addition of different reactive vapor as H_2O [4], O_2 [6], H_2 [7], solvent [6] influences the film microstructure. By reducing moderately the pressure in the reactor (LPCVD), a columnar morphology is observed and the films exhibit a higher porosity [8]. Depending on the properties aimed we can select the best microstructure and therefore the most appropriate CVD process.

Process	Temperature (°C)	Pressure (Torr)	Gas atmosphere	Growth rate (nm/min)	References
AP-CVD	350-700	760	N_2	1000	[4,5]
	300-550	760	N_2/H_2	1000	[7]
	350-500	760	N_2/H_2O	450	[4]
AA-CVD	450-650	760	N_2/acac/O_2	50-500	[6]
	450-600	760	N_2	1800	[6]
LP-CVD	300-600	1-20	N_2	40	[8]
CVI	300-400	1-20	N_2	10	[8,11]
DLI-CVD	350-450	6	N_2/O_2/Cu(tmhe)$_2$/xylene	60-200	unpublished
	410	6	N_2/O_2/Ag(piv)/solvent	55-115	unpublished

Table 1: Typical growth rate obtained using various CVD processes for the deposition of TiO_2 starting from TTIP as molecular precursor.

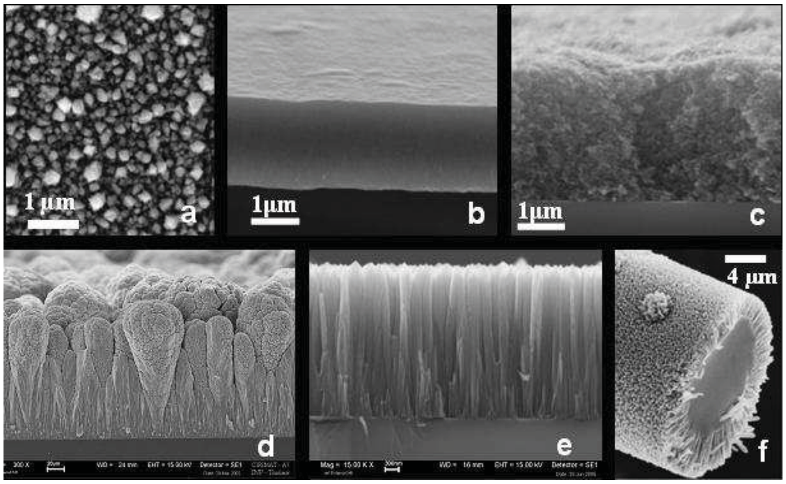

Fig. 1: Morphologies of TiO_2 layers grown by various CVD processes: (a) AP-CVD 550 °C/H_2; (b) AA-CVD TTIP/acac 500 °C; (c) AA-CVD TTIP/acac 650 °C; (d) LP-CVD 600 °C/10 Torr/20 % TTIP; (e) LP-CVD 400 °C/20 Torr/260 ppm TTIP ; (f) CVI 400 °C/20 Torr/76 ppm TTIP.

UV photocatalytic activity of TiO_2 on steel. TiO_2 films are deposited on steel to get self cleaning surfaces. This is achieved if the layer is highly hydrophilic and photocatalytically active. Fig. 2 shows that these properties are correlated since mechanisms of hydrophilicity involve photocatalysis. However the efficiency of photocatalysis depends on the micro- and nano-structural features of the film and on its purity. For instance, a strong contamination of carbon is a killer for photocatalysis as found for AA-CVD layers grown using acetyl acetonate (acac) as solvent (Fig. 3) [6]. Furthermore, photocatalysis is both a surface and a bulk property in the sense that electron-hole pairs are generated under irradiation in the bulk and chemical reactions involving for instance OH° radicals occur on the surface of anatase crystallites [9]. So there is a critical thickness for supported TiO_2 films to maximize photocatalysis (fig. 2) that is related to penetration depth of light (Fig. 4) [9,10].

Air treatment: TiO_2 on microfibers. For the photocatalytic treatment of gas effluent, TiO_2 growth on microfibers by chemical vapor infiltration (CVI) leads to high specific surface area as required (Fig. 1f) [8,11]. Doping of these layers is possible for activity in the visible range [12].

Visible photocatalytic activity: N-doping. Anionic doping is a great challenge to improve activity in the day light [13]. This was achieved using hydrazine as N source and correlations with the microstructural features were established and are summarized in Figures 5 and 6 [14].

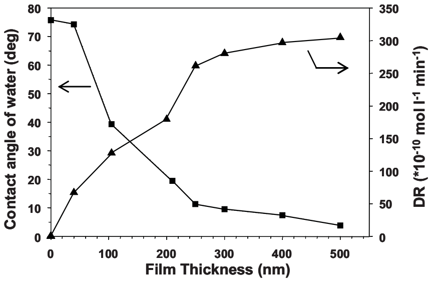

Fig. 2: Correlation between hydrophilicity and photocatalytic decomposition rate (DR) of Orange G aqueous solutions under UV irradiation (365 nm). The TiO_2 films were grown on stainless steel at 400 °C using 10^{-4} TTIP (reproduced with permission [5]).

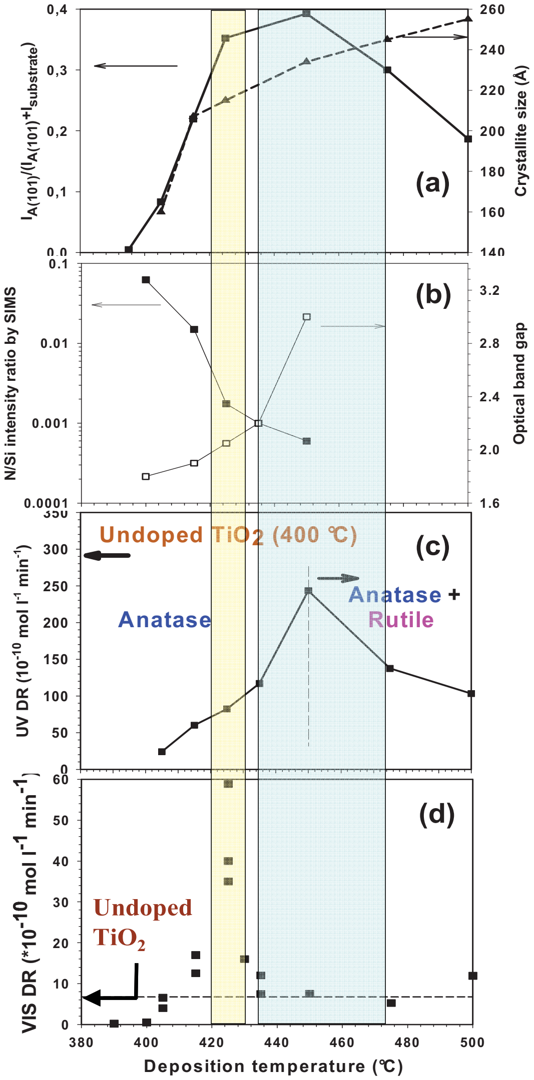

Fig. 5 : Influence of the deposition temperature of N-doped TiO_2 films (a) on the proportion of anatase relative to rutile and of the crystallite size of anatase; (b) on the relative nitrogen content and the optical band gap; (c) on UV photocatalytic decomposition rate of Orange G solutions and (d) on VIS photocatalytic decomposition rate of Orange G (λ > 400 nm). The regions of maximum visible and UV photocatalytic activity are colored to be correlated with microstructural features of the films. TiO_2 layers (~ 300 nm thick) were grown on stainless steel using N_2H_4/TTIP mole ratio = 25 (Reproduced with permission [14]).

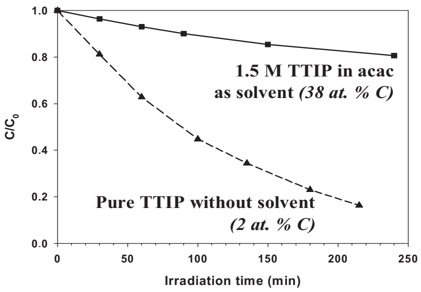

Fig. 3: Decomposition of Orange G aqueous solution vs UV light exposure by two TiO_2 samples (2500 nm thick) grown on steel at 500 °C by AA-CVD (pyrosol) without and with solvent (high C contamination).

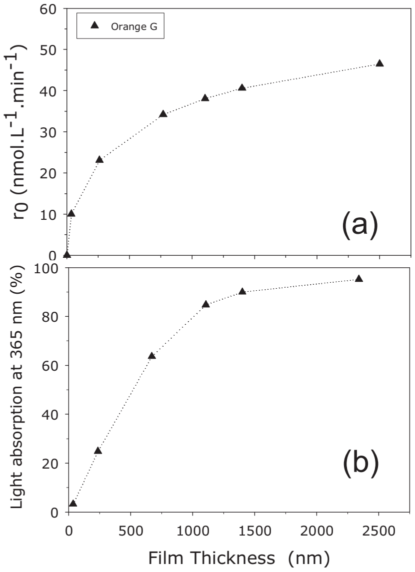

Fig. 4: Influence of TiO_2 film thickness on (a) the photocatalytic degradation rate of orange G aqueous solution and (b) the UV light absorption at 365 nm. TiO_2 were deposited at 400 °C, 20 Torr; 76-260×10^{-6} of TTIP on flat glass substrates.

Bactericidal surfaces: TiO_2-M (M = Ag, Cu) nanocomposite coatings. Multilayers TiO_2/Ag prepared by multi-step process were antibacterial after UV exposure [15]. Nanocomposite TiO_2-Ag layers grown by one step DLI-CVD exhibit durable bactericidal behavior for Ag nanoparticles content < 1 at.% (Fig. 7). Multifunctionality was observed with self cleaning (photocatalysis) and biocidal activity. Comparatively TiO_2-Cu coatings are bactericidal for higher Cu content (>3.5 at.%).

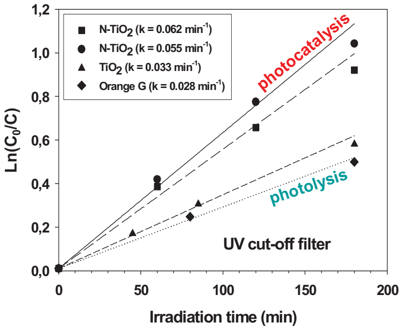

Fig. 6: Decomposition rate of Orange G aqueous solutions (10 ppm) under solar light using an UV cut-off filter by N-doped TiO_2 films (300 nm) grown on stainless steel at 425 °C using 100 ppm TTIP and N_2H_4/TTIP = 20 (■) and 25 (●). DR of Orange G with undoped TiO_2 and without TiO_2 (photolysis) are also shown (irradiation intensity 42 mW/cm^2).

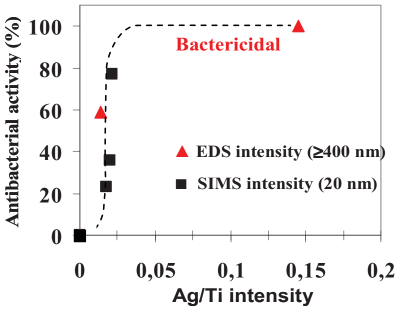

Fig. 7: Influence of the silver content of TiO_2-Ag nanocomposite coatings on the anti-bacterial activity (*S. aureus*).

Acknowledgements

The authors thank Drs. F.-D. Duminica, C. Sarantopoulos, L. Bedel and F.N. Renaud for their contribution. This work was partly supported by ANR under contract ANR-06-MAPR-0007-01.

References

[1] S. Popescu, I. Demetrescu, C. Sarantopoulos, A.N. Gleizes, D. Iordachescu, J. Mater. Sci.: Mater. Med., 19 (2008), p. 1451.

[2] W. Haenni, H.E. Hintermann, D. Morel, A. Simmen, J. Physique coll., C5-50 (1989), p. 401.

[3] G.A. Battiston, R. Gerbasi, M. Porchia, L. Rizzo, Chem. Vap. Deposition, 5 (1999), p. 73.

[4] F.-D. Duminica, F. Maury and F. Senocq, Surf. Coat. Technol., 188-189 (2004), p. 255.

[5] F.-D. Duminica, F. Maury and R. Hausbrand, Surf. Coat. Technol., 201 (2007), p. 9304.

[6] F.-D. Duminica, F. Maury and S. Abisset, Thin Solid Films, 515 (2007), p. 7732.

[7] F.-D. Duminica, F. Maury, R. Hausbrand, Proc. CVD 17, ECS Transaction, (2009) accepted.

[8] C. Sarantopoulos, A.N. Gleizes, F. Maury, Surf. Coat. Technol., 201 (2007), p. 9354.

[9] J.-M. Herrmann, Catalysis Today, **53** **(**1999), p. 115.

[10] M.L. Hitchman, F. Tian, J. Electroanal. Chem., 538-539 (2002), p. 165.

[11] C. Sarantopoulos, A. N. Gleizes, F. Maury, E. Puzenat, C. Guillard J.-M. Herrmann, Applied Catal. B, (accepted)

[12] C. Sarantopoulos, A. N. Gleizes and F. Maury, Thin Solid Films, (2009) doi: 10.1016/j.tsf.2009.04.070

[13] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki and Y. Taga, Science, 293 (2001), p. 269.

[14] F.-D. Duminica, F. Maury and R. Hausbrand, Surf. Coat. Technol., 201 (2007), p. 9349.

[15] L.A. Brook, P. Evans, H.A. Foster, M.E. Pemble, A. Steele, D.W. Sheel, H.M. Yates, J. Photochem. Photobio. A: Chem., 187 (2007), p. 53.

Electrochemistry and physical chemical methods

doi:10.4028/www.scientific.net/KEM.415

Chemical Vapor Deposition of TiO₂ for Photocatalytic Applications and Biocidal Surfaces

doi:10.4028/www.scientific.net/KEM.415.1

References

[I] S. Popescu, I. Demetrescu, C. Sarantopoulos, A.N. Gleizes, D. Iordachescu, J. Mater. Sci.:

Mater. Med., 19 (2008), p. 1451.
doi:10.1007/s10856-008-3405-6

[2] W. Haenni, H.E. Hintermann, D. Morel, A. Simmen, J. Physique coll., C5-50 (1989), p. 401.

[3] G.A. Battiston, R. Gerbasi, M. Porchia, L. Rizzo, Chem. Vap. Deposition, 5 (1999), p. 73.
doi:10.1002/(SICI)1521-3862(199903)5:2<73::AID-CVDE73>3.0.CO;2-L

[4] F.-D. Duminica, F. Maury and F. Senocq, Surf. Coat. Technol., 188-189 (2004), p. 255.
doi:10.1016/j.surfcoat.2004.08.038

[5] F.-D. Duminica, F. Maury and R. Hausbrand, Surf. Coat. Technol., 201 (2007), p. 9304.
doi:10.1016/j.surfcoat.2007.04.011

[6] F.-D. Duminica, F. Maury and S. Abisset, Thin Solid Films, 515 (2007), p. 7732.
doi:10.1016/j.tsf.2007.03.057

[7] F.-D. Duminica, F. Maury, R. Hausbrand, Proc. CVD 17, ECS Transaction, (2009) accepted.

[8] C. Sarantopoulos, A.N. Gleizes, F. Maury, Surf. Coat. Technol., 201 (2007), p. 9354.
doi:10.1016/j.surfcoat.2007.04.073

[9] J.-M. Herrmann, Catalysis Today, 53 (1999), p. 115.
doi:10.1016/S0920-5861(99)00107-8

[10] M.L. Hitchman, F. Tian, J. Electroanal. Chem., 538-539 (2002), p. 165. [II] C. Sarantopoulos, A. N. Gleizes, F. Maury, E. Puzenat, C. Guillard J.-M. Herrmann, Applied Catal. B, (accepted)
doi:10.1016/S0022-0728(02)01252-4

[12] C. Sarantopoulos, A. N. Gleizes and F. Maury, Thin Solid Films, (2009) doi: 10.1016/j.tsf.2009.04.070

[13] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki and Y. Taga, Science, 293 (2001), p. 269.
doi:10.1126/science.1061051
PMid:11452117

[14] F.-D. Duminica, F. Maury and R. Hausbrand, Surf. Coat. Technol., 201 (2007), p. 9349.
doi:10.1016/j.surfcoat.2007.04.061

[15] L.A. Brook, P. Evans, H.A. Foster, M.E. Pemble, A. Steele, D.W. Sheel, H.M. Yates, J. Photochem. Photobio. A: Chem., 187 (2007), p. 53.
doi:10.1016/j.jphotochem.2006.09.014