Fractal TiO_2 nanostructures by non-thermal laser ablation at ambient pressure

Emanuele Cavaliere[1], Gabriele Ferrini[1], Pasqualantonio Pingue[2] and Luca Gavioli[1]

1 Interdisciplinary Laboratories for Advanced Materials Physics (i-LAMP) & Dipartimento di Matematica e Fisica, Università Cattolica del Sacro Cuore, via dei Musei 41, I-25121 Brescia, Italy
2 Laboratorio NEST, Scuola Normale Superiore, Piazza San Silvestro 12, 56127 Pisa, Italy
e.cavaliere@dmf.unicatt.it

Abstract

Titanium dioxide (TiO_2) is one of the most relevant strategic material in many technologically important areas, like heterogeneous catalysis [1-3], photo-assisted oxidation [4], optical [5,6] and photovoltaic devices [7]. To increase the efficiency of these processes through material engineering, routes such as tailoring the absorption edge of the material in the visible light range [8-11], or maximizing the effective surface area are available. A fundamental contribution to the latter may come from realization of fractal materials [12] with nano- and mesoscopic pores, or by hierarchical organization of nanostructures [13,14], enhancing, for instance, the selectivity behavior of catalyst material with high porosity [15]. The synthesis by pulsed laser deposition (PLD) using nanosecond (ns) laser pulses resulted in the formation of nanoparticles (NP) either in low [16], high [17-21,27] or ultra-high vacuum [22], and even in liquid [23], while formation of dendritic-like structures has been reported only for ns-PLD in water [28] or at high argon pressure by employing thousands of ns pulses [24]. Recently, femtosecond (fs) pulsed laser deposition (fs-PLD) has drawn a lot of interest due the process of non-thermal ablation, resulting from the high-energy density and short time-width of the pulse that bring the target surface to a supercritical state [25,26]. It has been shown that laser fluence, sample-target distance and environment pressure influence the properties of the deposited material [27-30], but up to now very little is known about TiO_2 nanostructure formation at ambient pressure, both for fs and ns regime. In this work we demonstrate that ambient pressure fs-PLD allows to obtain fractal TiO_2 nanostructures in crystalline form at room temperature (Figure 1). These structures were studied by scanning electron microscope (SEM), Raman spectroscopy and X-Ray photoemission spectroscopy (XPS). We show that the dendritic aggregations on silicon wafers at room temperature (RT) have a Hausdorff-Besicovich dimension [31] of 1.56, and are hence fractals. The fractals are composed by nanoparticles with an average diameter smaller than 20 nm, with the presence of larger NP with a diameter above 50 nm. We show that the fractal dimension depends on the density of deposited material, while the size distribution of the fractals and NP depends on laser fluence and sample/target distance (Figure 2). XPS shows that the as-deposited nanostructures are TiO_2 while Raman spectroscopy reveals that the crystalline structure of fractals and NP is composed by both rutile and anatase phase.

Figures

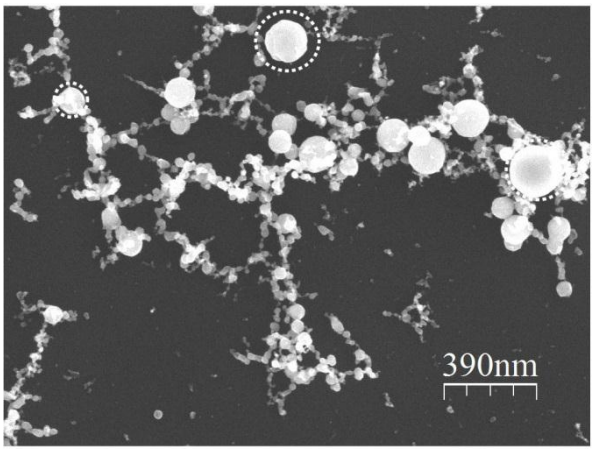

Figure 1. SEM image taken at 10 KeV beam energy. The material was deposited with 150 laser pulses at a 9.6 J/cm^2 laser fluence and substrate-target distance of 2 mm. It is possible to distinguish few large nanoparticles with a circular-like shape and aggregates presenting a dendritic shape. The dark background is the silicon wafer substrate. Some of the large NP have been highlighted by dotted circles to evidence the crystalline shape.

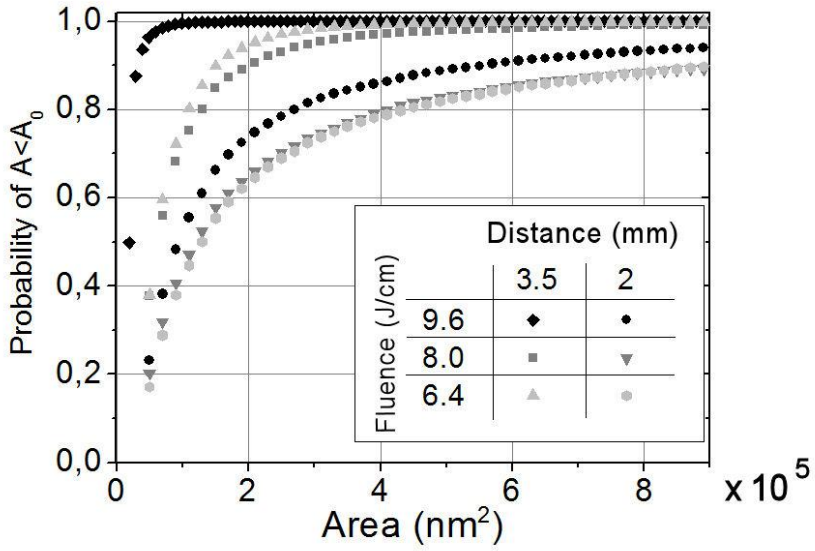

Figure 2. Probability of finding a nanostructure with an area $A < A_0$ as a function of laser fluence and sample/target distance. Smaller fractals are found at higher laser fluences, and at 3.5 mm sample/target distance.

References

[1] D.W. Flaherty *et al.* J. Phys. Chem. C **111** (2007**)** 4765.
[2] I.N. Remediakis, N. Lopez, J.K. Norskov, Angew. Chem., Int. Ed. **44** (2005**)** 1824.
[3] A. Kubacka, M. Fernández-García, G. Colón, Chem. Rev. **112** (2012**)** 1555.
[4] C.G. Wu, C.C. Chao, F.T. Kuo, Catalysis Today **97** (2004) 103.
[5] H.Y. Zheng, H.X. Qian,W. Zhou, Appl. Surf. Sci. **254** (2008) 2174.
[6] A. Pillonnet *et al.*, J. Luminescence **119** (2006) 560.
[7] W.X. Que, A. Uddin, X. Hu, J. Power Sources **159** (2006) 353.
[8] M. Chiodi, C.P. Cheney, P. Vilmercati, E. Cavaliere, N. Mannella, H.H. Weitering, L. Gavioli, J. Phys. Chem. C 116 (2012) 311
[9] A. N. Mangham *et al.*, J. Phys. Chem. C 115 (2011) 15416
[10] W. J. Yin *et al.*, Phys. Rev. B 82 (2010) 045106
[11] A. Kubacka, M. Fernandez-García, and G. Colon, Chem. Rev. 2012, 112, 1555-1614
[12] F. Gassmann, R. Kotz and A. Wokaun, Europhysics News 34, 176 (2003)
[13] Rolison D R 2003 Science 299 1698
[14] F. Di Fonzo *et al.*, Nanotechnology 20 (2009) 015604
[15] S.P. Rigby and L.F. Gladden, J. of Catalysis **180**, 44 − 50 (1998)
[16] M. Filipescu *et al.*, Appl. Surf. Sci. 253 (2007) 8258
[17] M. Sanz *et al.*, Appl. Phys. A 101, 639 (2010)
[18] S. Noel, J. Hermann and T. Itina, Appl. Surf. Sci. 253, 6310 − 6315 (2007)
[19] U. Chakravarty *et al.*, J. of Appl. Phys. 108, 053107 (2010)
[20] S. Eliezer *et al.*, Phys. Rev. B 69, 144119 (2004)
[21] J.C. Alonso *et al.*, App. Surf. Sci 255 (2009) 4933
[22] D. Cattaneo, N. Righetti, C.S. Casari, A. Li Bassi and C.E. Bottani, Appl. Surf. Sci. 253, 7917 (2007)
[23] P.V. Kazakevich, A.V. Simakin, V.V. Voronov, G.A. Shafeev, Appl. Surf. Sci. 252 (2006) 4373
[24] P.L. Ong *et al.*, Appl. Surf. Sci. 254, 1909 (2008)
[25] P. Lorazo, L. J. Lewis and M. Meunier, Phys. Rev. B 73, 134108 (2006)
[26] D. Perez, L.J. Lewis, Phys. Rev. B 67, 184102 (2003)
[27] S. Amoruso, G. Ausanio, R. Bruzzese, M. Vitiello, and X. Wang, Phys. Rev. B 71 33406 2005
[28] O. R. Musaev, A. E. Midgley, J. M. Wrobel, J. Yan, M. B. Kruger, J. Appl. Phys. 106, 054306, 2009
[29] H. Köster, K. Mann, Appl. Surf. Sci. 109/110, 428 − 432 (1997)
[30] S. Amoruso, R.Bruzzese, X.Wang and J. Xia, Appl. Phys. Lett. 92, 041503 (2008)
[31] H. M. Hastings and G. Sugihara, *Fractals*, Oxford University Press, New York, 1993.