Supplementary Material (ESI) for Journal of Materials Chemistry

Supporting information

Experimental

Evaporation of the individual TiO_2 and SiO_2 layers was carried out in an electron bombardment evaporator by using TiO or SiO_2 pellets as a target. Quartz plates or pieces of a Si (100) wafer with a size of 2.5x2.5 cm^2 were used as substrates. Quite homogenous multilayer films were obtained over the whole substrate area. The distance between the evaporation source and the substrate position was 50 cm. Deposition was carried out at room temperature and the 1DPCs structures were used without any further treatment after their preparation. Stoichiometric and columnar layers of TiO_2 and SiO_2 were obtained by performing the evaporation in 10^{-4} torrs of O_2 by placing the substrates at a glancing zenithal angle α which was varied with respect to the evaporator source from 60º to 85º, depending on the experiment. These glancing geometries produce films with a tilted columnar microstructure.[1-5] Individual layers with a thickness comprised between 70 and 120 nm for TiO_2 and for SiO_2 were prepared by this method. The individual layer thickness was controlled by monitoring the evaporation process with a quartz crystal monitor previously calibrated by comparing its response with the thickness of individual films of either TiO_2 or SiO_2. All thin films were prepared at a rate comprised between 0.5 and 1.5 Å/s. A characteristic of these individual layers is their high porosity and, consequently, a much lower refractive index than the corresponding bulk materials.[6,7]

Successive and alternated layers of TiO_2 (1st, 3rd, 5th, etc.) and SiO_2 (2nd, 4th, 6th, etc.) were prepared by changing the azimuthal orientation of the substrate φ between 0º, 90º, 270º or 180º at each deposition.

The microstructure of the porous 1DPC structures deposited on a silicon wafer was examined by Field Emission Scanning Electron Microscopy (FESEM) in a Hitachi S5200 microscope. Cross sectional views were obtained by cleaving the silicon substrates.

The quasi-normal incidence reflectance spectra of SiO_2-TiO_2 1DPCs structures deposited on glass were measured with a Bruker IFS-66 FTIR spectrophotometer attached to a microscope with a 4X objective with 0.1 of numerical aperture (light cone angle ± 5.7º).

The optical and microstructural parameters for the samples in Figure 3 are the following: a) the refractive indexes are n_{TiO2}=1.75 and n_{SiO2}=1.24 in all cases; b) the thicknesses of the constituent layers are, from left to right in the figure, t_{SiO2}=t_{TiO2}=75 nm, t_{SiO2}=t_{TiO2}=83 nm, t_{SiO2}=t_{TiO2}=90 nm, t_{SiO2}=t_{TiO2}=98 nm, t_{SiO2}=t_{TiO2}=106 nm, t_{SiO2}=t_{TiO2}=127 nm, respectively; c) the microstructure is defined by the azimuthal angles ϕ_{TiO2}=ϕ_{SiO2}=0º for the first tree samples; ϕ_{TiO2}=0º, ϕ_{SiO2}=180º for the next two; and by a sequence of rotations of the sort ϕ_{TiO2}=0º, ϕ_{SiO2}=90º, ϕ_{TiO2}=180º, ϕ_{SiO2}=270º, for the last one.

Layer parameters (refractive index and thickness) were estimated by modeling the optical behavior of the stacked structure with a software code based on the scalar wave approximation. The same software was used to estimate the changes in refraction index of the TiO_2 and SiO_2 layers leading to variations in the position of the reflecting maxima when the PBDM structures are infiltrated with liquids. The infiltration capacity of the films was tested by immersing them into liquids of different refraction indices (n), in the present case been employed water (1,333), isopropanol (1,432), toluene (1,497) and Cl-benzene (1,525). The optical response of the porous 1DPC was monitored by looking at the position of its reflectance maxima.

1 M. J. Brett and M. M. Hawkeye, *Science,* 2008, **319**, 1192.

2 M. M. Hawkeye and M. J. Brett, *J. Vac. Sci. Technol.* A, 2007, **25**, 1317.
3 K. Robbie and M. J. Brett, *J. Vac. Sci. Technol. A,* 1997, **15**, 1460.
4 S. Wang, G. Xia, H. He, K. Yi, J. Shao and Z. Fan, *J. Alloys Compd.,* 2007, **431**, 287.
5 G. Kiema, M. J. Colgan, M. J. Brett, *Sol. Energy Mater. Sol. Cells,* 2005, **85**, 321.
6 J.R. Sánchez-Valencia, A.Borrás, A. Barranco, V.J. Rico, J.P. Espinós, A.R. González-Elipe, *Langmuir* 2008, **24**, 9460.
7 A. Borrás, J.R. Sánchez-Valencia, J. Garrido-Molinero, A. Barranco, A.R. González-Elipe, *Microporous and Mesoporous Materials* 2009, **118,** 314

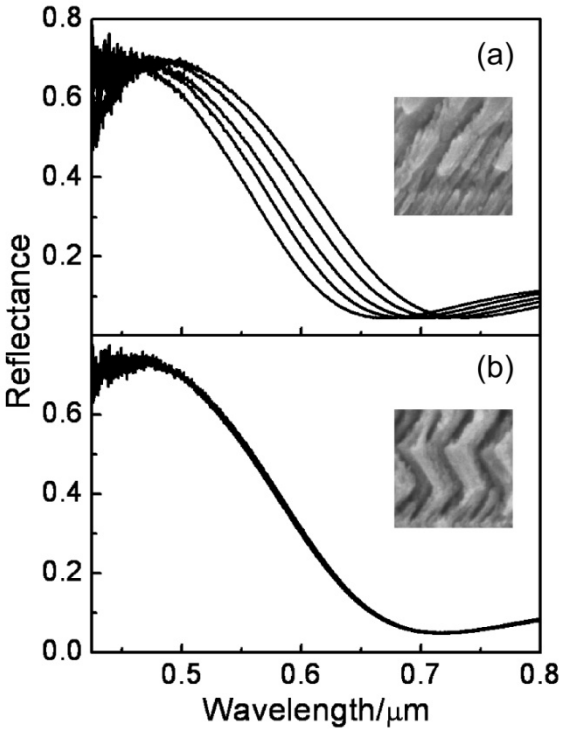

Figure S1. Series of normal incidence specular reflectance spectra measured from 100μmX100μm area spots, separated two millimeter from each other, along a line on the surface of two different multilayers. In both cases, zenithal deposition angles were set to α_{TiO2}=60º and α_{SiO2}=85º, while azimuthal deposition angles were varied: (a) ϕ_{TiO2}=ϕ_{SiO2}=0º; (b) ϕ_{TiO2}=0º,ϕ_{SiO2}=180º. The better uniformity of the samples prepared using the latter experimental conditions can be appreciated. SEM micrographs included as insets show details of the cross sections of the two samples.

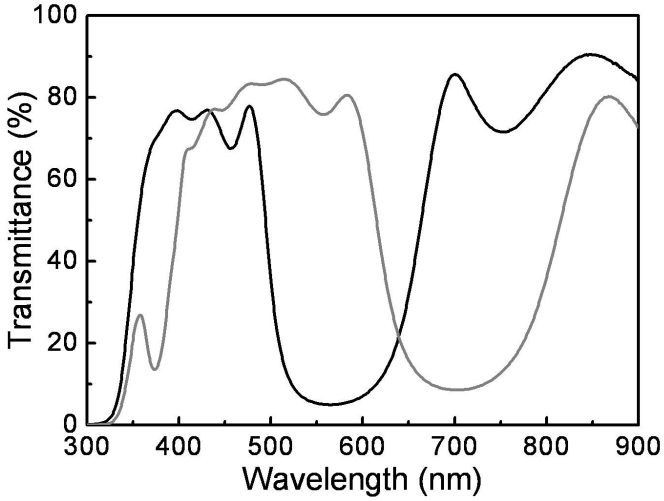

Figure S2. Transmittance spectra of two multilayered samples with the 11 stacked layers and different reflection peaks position. The samples correspond with the experimental conditions: ϕ_{TiO2}=0º,ϕ_{SiO2}=180º, α_{TiO2}=α_{SiO2}=60º and t_{TiO2}=t_{SiO2}=90 nm (black) and ϕ_{TiO2}=0º,ϕ_{SiO2}=180º, α_{TiO2}=α_{SiO2}=70º and t_{TiO2}=t_{SiO2}=112 nm (grey). Note that despite their different profiles and position of the reflectivity maxima, the two spectra present quite equivalent transmittances in the regions outside the minimum of the transmittance curves.

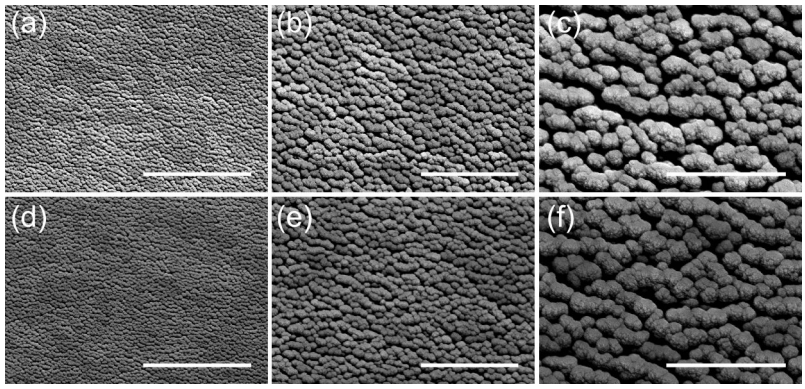

Figure S3. Superficial electron microscopy images of TiO_2-SiO_2 multilayers deposited on silicon wafer (100) by GLAD using ϕ_{TiO2}=0º,ϕ_{SiO2}=180º and α_{TiO2}=α_{SiO2}=80º before (up) and after (down) their infiltration with water. Note that no alteration of the columnar structure has been provoked by surface tension effects. The scale bar is 5 μm for (a) and (d), 2 μm for (b) and (e) and 1 μm for (c) and (f).