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Tuning the Selectivity and Sensitivity of Mesoporous Dielectric Multilayers by modifiying the Hydrophobic/Hydrophilic Balance of the Silica Layer

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Supporting Information

The open porosity was measured from the change of the optical characteristics (n: refractive index, k: extinction coefficient). The Lorentz-Lorenz equation is used for the characterization of porous substrates with ellipsometric porosimetry [1]:

An empty porous substrate with the refractive index n_e (n_{air} = 1, V = volume of open pores):

$$P_{ve} = \frac{n_e^2 - 1}{n_e^2 + 2} = V \times \frac{n_{air}^2 - 1}{n_{air}^2 + 2} + (1 - V) \times \frac{n_d^2 - 1}{n_d^2 + 2} = (1 - V) \times \frac{n_d^2 - 1}{n_d^2 + 2} \quad (1)$$

A filled porous substrate with the refractive index n_f (n_{ads} = refractive index of the adsorbate):

$$P_{vf} = \frac{n_f^2 - 1}{n_f^2 + 2} = V \times \frac{n_{ads}^2 - 1}{n_{ads}^2 + 2} + (1 - V) \times \frac{n_d^2 - 1}{n_d^2 + 2} \quad (2)$$

When the refractive index of the filled and empty porous substrates is known, one can determine the porosity of the material without knowing the refractive index of the dense material:

$$P_{vf} - P_{ve} = \frac{n_f^2 - 1}{n_f^2 + 2} - \frac{n_e^2 - 1}{n_e^2 + 2} = V \times \frac{n_{ads}^2 - 1}{n_{ads}^2 + 2} \quad (3)$$

Thus, the volume V_{ads} of the open pores can be determined as follows:

$$V_{ads} = \frac{n_f^2 - 1}{n_f^2 + 2} - \frac{n_e^2 - 1}{n_e^2 + 2} \Big/ \frac{n_{ads}^2 - 1}{n_{ads}^2 + 2} \quad (4)$$

The adsorption-desorption isotherm V_{ads} vs RH (Relative humidity) was then determined by fitting the n =F(RH) curve at each RH in order to determine open porosity of the water-saturated mesoporous films. The open porosity measured for titania films grown on silica layers which have variable hydrophilic/hydrophobicbalance is shown in Fig. 1:

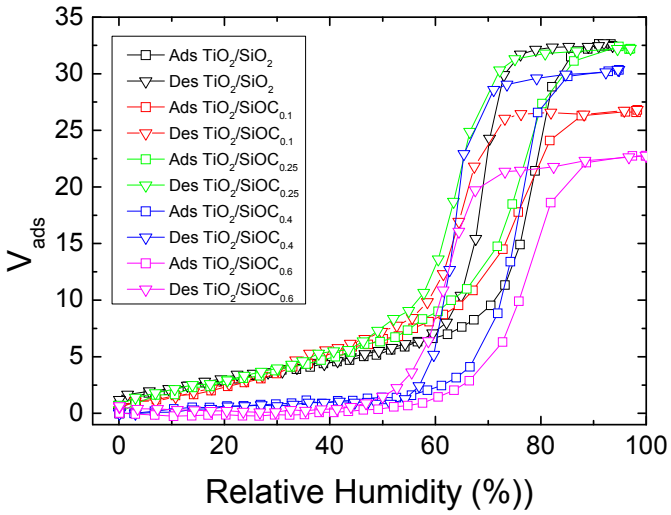

Figure 1 : Adsorption-desorptions isotherms of titania films grown at silica films with variable hydrophilic/hydrophobic balance obtained by Lorentz-Lorenz equation

The results depicted in Fig.1 show that the open porosity of the films varies from 32.6% for TiO_2 grown on SiO_2 to 26,8 % for TiO_2/SiOC0,6. The open porosity remains close to ~30 % when the MTES/TEOS ratio increase up to 0,25, and a decrease of it was observed over that value. Therefore, the adsorption-desorption isotherm show an identical hysteresis loop for all samples, suggestion identical mesostructure for all of them. This result suggests that no change of the mesostructure of the titania films was occurred.

According to the result presented in Fig.1, we assume that the titania films remain porous whatever the silica film without change of the mesostructure. This means that existence of −OH groups were enough for mesoporous titania film whatever the MTES/TEOS ratio used for the silica layer.

The adsorption desorption isotherm obtained by fitting by fitting the n=F(RH) curve suggested that the open porosity is 32.6 % and 36 % respectively for TiO_2 and SiO_2.

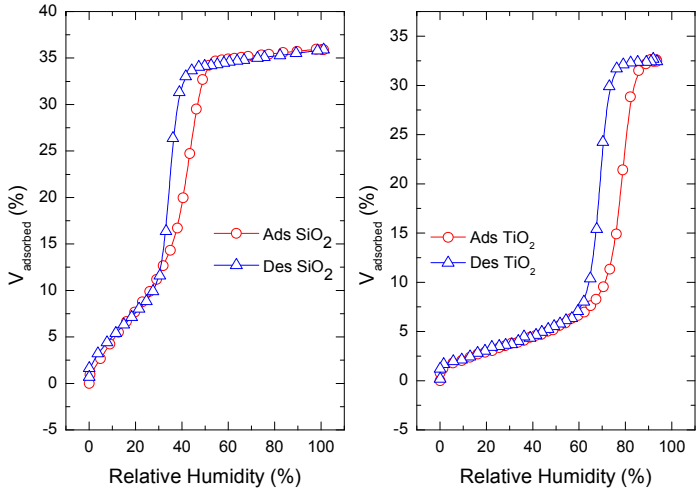

Figure 2 : Adsorption-desorptions isotherms of titanium and silica films coated glass obtained by Lorentz-Lorenz equation

Table 1 : Film thicknesses extracted from SEM cross-sectional images shown in Figure 5

Thickness (nm)	SiO_2/TiO_2	$SiC_{0.1}/TiO_2$	$SiC_{0.25}/TiO_2$	$SiC_{0.4}/TiO_2$	$SiC_{0.6}/TiO_2$
Silica 1	72.7	70.6	45.6	44.7	46.6
Titanium 2	93.7	87.4	79	85.7	76.4
Silica 3	76.4	69.7	50.5	47	43.7
Titanium 4	87.6	93.2	82	85.7	87.8
Silica 5	74.6	74	40.7	42.9	35.7
Titanium 6	80.2	85.4	85.1	82	78.3

[1] Baklanov and Mogilnikov, Microelectron. Eng. 2002, 64, 335; Eslava et al., Langmuir 2007, 23, 12811