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Colloidal approach to Au-loaded TiO_2 thin films with optimized optical sensing properties

Electronic Supplementary Information

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Spectroscopic ellipsometry measurements in different environments

Spectroscopic ellipsometry analyses performed on thin films under different environments allow the estimation of the open porosity and the refractive index of the material composing the films, as reported in the literature[1]. In fact the refractive index of nanocrystalline or amorphous material can be different from that of bulk crystalline material, leading to incorrect porosity determinations. These analyses have been performed on TG4 and TGP4 samples under air and ethanol with a custom built cell provided with a sample holder and with inlet and outlet allowing to perform multiangle spectroscopic ellipsometry measurements in different environments (both gaseous and liquid). The experimental complex dielectric functions can be approximated with linear effective medium approximation (EMA) models as follows:

$\varepsilon_A = (1 - P)\varepsilon_{A,matrix} + P\varepsilon_{A,pores}$

$\varepsilon_E = (1 - P)\varepsilon_{E,matrix} + P\varepsilon_{E,pores}$

where A, E and P stand for air, ethanol and pores volume fraction, respectively, and ε is the complex dielectric function ($\varepsilon=\varepsilon_1+i\varepsilon_2$). The linear EMA relationship is a simple model that has been used to obtain an estimation of the dielectric functions of the matrix. In the two equations, the epsilon value of the matrix is the same, because the matrix dielectric constants are not affected by performing the measurements in different media, while the epsilon values of the pores filled with air and ethanol are basically the values for air and ethanol respectively, assuming than the two media fill completely the pores; according to these observation, by combining the two equations it is possible to eliminate the pores volume fraction P and calculate the complex dielectric function of the matrix ε_{matrix} as a combination of known parameters:

$$\varepsilon_{matrix} = \frac{\varepsilon_E \varepsilon_{A,pores} - \varepsilon_A \varepsilon_{E,pores}}{\varepsilon_E + \varepsilon_{A,pores} - \varepsilon_A - \varepsilon_{E,pores}}$$

If considering a wavelength range in which all media and samples are not absorbing (so $\varepsilon_2 = 0$), the previous equation can be simplified as the following:

$$n_{matrix} = \sqrt{\frac{n_E^2 n_{A,pores}^2 - n_A^2 n_{E,pores}^2}{n_E^2 + n_{A,pores}^2 - n_A^2 - n_{E,pores}^2}}$$

This estimation gives a lower limit for the refractive index of the matrix, since only the open pores are accessible by the ethanol, and also the pores may be only partially filled with it.

Having now a more reliable refractive index of the matrix, this value can be used to evaluate the porosity of the film through EMA models considering only the refractive index measured in air.

Since the linear EMA is a simple but sometimes a rough approximation for porosity evaluation, it has been presented here only for the estimation of the dielectric constants of the matrix, but the porosity of the samples prepared in this study has been evaluated with the Bruggeman model[2], a more reliable function for porosity determination.

Figure 1 shows the refractive index dispersion curves for TG4 and TGP4 samples under air (black line) and ethanol (grey line): the refractive index measured in ethanol is higher compared to air, because ethanol has a higher refractive index compared to air (1.36 compared to 1).

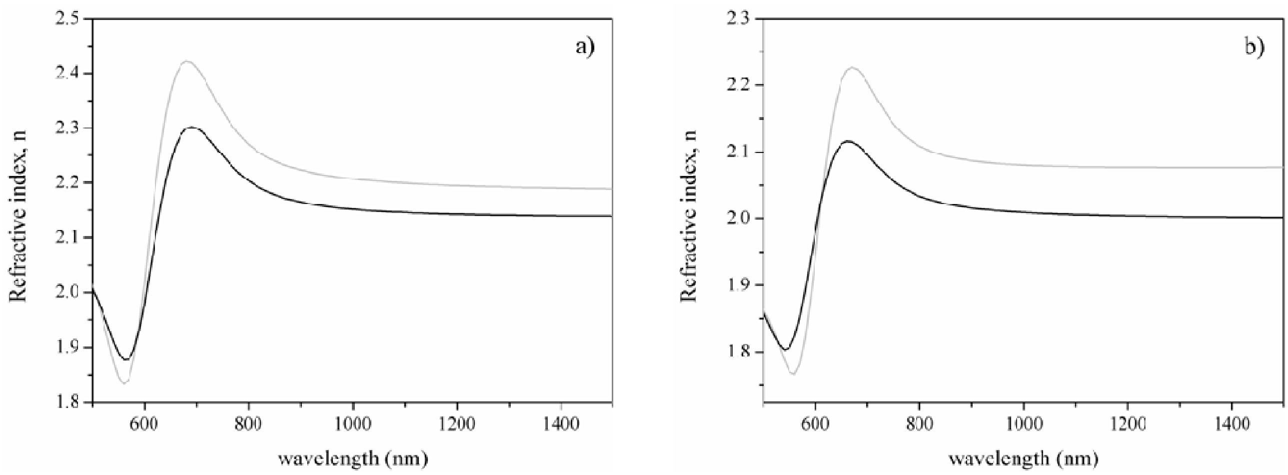

Figure 1. Refractive index dispersion curves of TG4 film (a) and TGP4 film (b) measured in air (black lines) and in ethanol (grey lines).

Using the procedure presented before, the refractive index of the TiO_2-anatase matrix has been evaluated. A value of 2.422 has been obtained for the TG4 sample and a value of 2.393 for the TGP4 sample. The two values are very similar, so as refractive index of the TiO_2 anatase matrix at 1100nm it has been used 2.408, corresponding to the mean value of the two.

With this corrected value, the effective pore volume fraction has been calculated and all the results are reported in Table 1: the porosity is slightly reduced when using the experimental refractive index for dense anatase instead of 2.44, the value reported in literature for fully dense anatase at 1100 nm[3,4], confirming that a small change in refractive index of nanocrystalline material compared to bulk material is occurring. Nevertheless, the variation between the two porosity estimations is relatively small.

Table 1. Estimated porosity of Au-loaded samples through the Bruggeman EMA model, using as refractive index of the TiO_2-anatase matrix at 1100 nm the theoretical value of 2.44 or the experimental value of 2.408.

Sample	Average porosity (%)	
	Theoretical	Experimental
TG3	22	20
TGP3	31	30
TG4	20	18
TGP4	29	27
TG5	11	9
TGP5	21	19

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