Au and Ag nanoparticle-doped-TiO_2 thin films: structural and optical characterization and antireflective properties

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Metal-dielectric nanocomposite (MNC) thin films have attracted much attention in the last years due to its unique electromagnetic behavior and high potential in diverse fields like photovoltaics [1] and sensing [2], other than metamaterials, photodetectors, catalysis, sub-wavelenght imaging, etc. The special electromagnetic properties of the MNC are primarily dominated by the localized surface plasmon resonance (LSPR) typical of noble metal nanoparticles (NPs). The control of the size, shape and density of these NPs embedded in a given solid matrix is needed for most of these applications.

Embedded in-situ Au nanoparticles (NPs) in solid dielectric matrices of SiO_2 and TiO_2 has been recently developed using a sol-gel method implemented for spin-coating deposition. The average diameter and the density of the NPs can be changed varying the metal precursor concentration. Larger Au NPs (of around 40 nm) can be obtained in TiO_2 films than in SiO_2 (around 13 nm) [3], this may be important for photovoltaic (PV) applications, because light scattering predominates over light absorption for larger metal NPs. After a treatment with a weak wet-chemical etching, formation of a pores structure in the film takes place, which is translated, for films deposited over Si substrates, in a strong anti-reflectance effect in comparison with non-etched films, meanwhile an intensity decrease and blue shift of the extinction spectra is clearly appreciable for samples deposited over glass substrates (fig. 1); this is consistent with the formation of the porous structure developing from the film surface towards the Si-interface, because the overall refractive index decrease over the curve measured by ellipsometry before etching.

More recently, we have extended this method to the case of Ag NPs by varying the metal precursor concentration [5]. The structural characterization, performed by HRTEM, HAADF-STEM, SEM and AFM techniques, reveals a succesful formation of Ag NPs inside and onto the film surface (figs. 2a-b). Optical measurements (reflectance, extinction, ellipsometry) have been performed, revealing a LSPR extinction peak appearing at ~520 nm, due to the high effective medium dielectric function. Again, if we apply a similar wet-chemical etching process explained above, a minimum in the overall reflectance curve will be observed (fig. 2c), making these films good candidates for antireflective coatings in PV applications, due to the low cost of making solar cells using silver rather than gold. In both cases the method is simple, easy to scale up and enables a certain control over size and density of NPs by changing the precursor concentrations, humidity and temperature.

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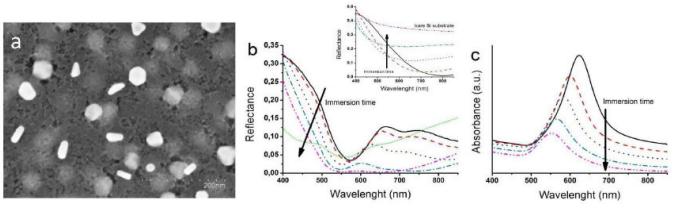

Figure 1: a) Planar view SEM image of etched Au-NPs/TiO_2 thin film, b) reflectance spectra (film deposited over Si substrate) with different times of etching (in the inset, the reflectance of an etched TiO_2 bare layer), c) extinction spectra of the same film (deposited over glass substrate).

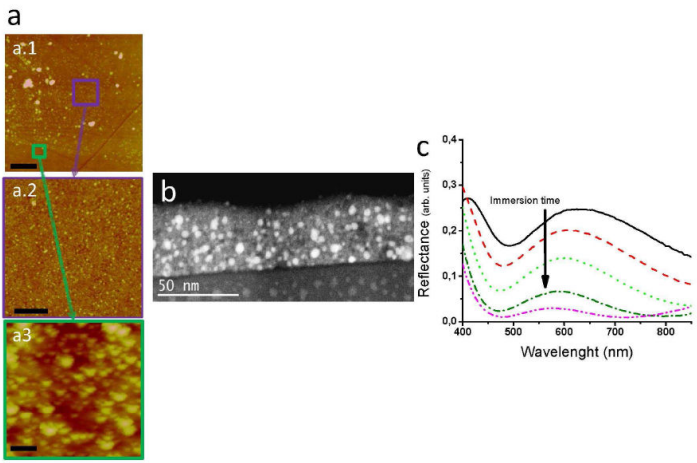

Figure 2: a) AFM images with different zooms of the surface of a Au-NPs/TiO_2 thin film (the black line represents the scale of a.1) 2 µm, a.2) 500 nm and a.3) 100 nm). b) HAADF-STEM cross section image showing the Ag NPs inside the layer. c) Reflectance spectra of film when it is applied the wet chemical etching process.