Nanoporous gold thin films deposited by magnetron sputtering: tayloring the porosity

R. Álvarez[1], **J. M. García-Martín**[2], M. Macías-Montero[1], L. Gonzalez-Garcia[1], J.C. González[1], V. Rico[1], J. Perlich[3], J. Cotrino[1,4], A. R. González-Elipe[1] and A. Palmero[1]

[1] Instituto de Ciencia de Materiales de Sevilla (CSIC-US), Americo Vespucio 49, 41092 Seville, Spain
[2] IMM-Instituto de Microelectrónica de Madrid (CNM-CSIC), Isaac Newton 8, 28760 Tres Cantos, Spain
[3] HASYLAB at DESY, Notkestrasse 85, 22603 Hamburg, Germany
[4] Departamento de Física Atómica, Molecular y Nuclear, University of Seville, 41071 Seville, Spain
jmiguel@imm.cnm.csic.es

Abstract

Nanoporous gold has attracted much attention in the science and technology for its high catalytic activity towards oxidation reactions, which equals that of gold nanoparticles but avoiding the problems of coarsening with a longer life time. A key element for this functionality is the possibility of synthesizing gold thin films with large surface area with valleys that penetrate deep into the material. Although nanoporous gold has usually been synthesized by chemical dealloying, the possibility of using plasma-assisted deposition techniques is highly desirable, not only because it might allow a better control on the surface and pore percolation features, but also from environmental and industrial points of view. In this context, we have studied the growth of nanoporous gold thin films by magnetron sputtering at room temperature and analyze the percolation depth and connectivity of the pores that penetrate into the film for enhanced catalytic applications [1, 2].

We have deposited gold thin films by magnetron sputtering at oblique angles using a wide range of values of the substrate tilt angle, σ, and the background pressure, p_g. We have analyzed the nanostructure of the obtained films by using different characterization techniques such as Atomic Force Microscopy (AFM), Field Emission Scanning Electron Microscopy (FESEM) and Grazing Incidence Small-Angle X-ray Scattering (GISAXS). We have also developed a Monte Carlo growth model, which accurately reproduces the experimental nanostructures. We have found that the whole set of deposited films can be categorized through only four generic nanostructures (see Fig. 1):

i) α-type (low σ, low p_g): the film is compact without any well defined geometrical pattern in the bulk of the material, and has a very small density of nanopores.

ii) β-type (intermediate σ, low p_g): the film is rather compact, but surface valleys percolate from the very surface of the film to near the substrate through vertical tilted mesopores. This structure could also be seen as a tilted highly coalescent columnar structure (i.e., columns are always touching), whereas mesopores can be devised as the empty space between the coalescent columns.

iii) γ-type (high σ, low p_g): The film possesses similarities with the β-type microstructure, but now surface valleys and mesopores are larger and the columns appear well separated and isolated from each other. For instance, Fig. 2 shows the GISAXS spectra of γ-type films with high σ: the off-center maxima in Π incidence indicate the existence of individual elements where a clear correlation distance can be determined.

iv) δ-like (any σ, high p_g): this film is characterized by vertical coalescent column-like structures, with a high density of nano- and mesopores occluded in the material, and with cavern-like surface patterns elongated in the vertical direction that penetrate deep into the bulk.

With the help of Monte Carlo simulations we have demonstrated that the main structuring mechanisms are the elastic scattering of the gold atoms on plasma heavy particles and the self-shadowing mechanism on the sample surface. Moreover, particular attention has been paid to the development of geometrical patterns in the bulk of the films as well as to the size and percolation depth of surface valleys, an aspect that has deserved little attention in previous studies in the literature for plasma-assisted depositions of thin films. Overall we have found that some of these nanostructures possess large surface area with high connectivity among nano- and mesopores, features that make plasma-assisted techniques an alternative to wet chemistry techniques to synthesize nanoporous gold thin films.

References

[1] J.M. Garcia-Martin, R. Alvarez, P. Romero-Gomez, A. Cebollada and A. Palmero, Appl. Phys. Lett. **97**, 173103 (2010)

[2] R. Alvarez, J. M. García-Martín, M. Macías-Montero, L. Gonzalez-Garcia, J. C. González, V. Rico, J. Perlich, J. Cotrino, A. R. González-Elipe and A. Palmero, Nanotechnology **24**, 045604 (2013)

Figures

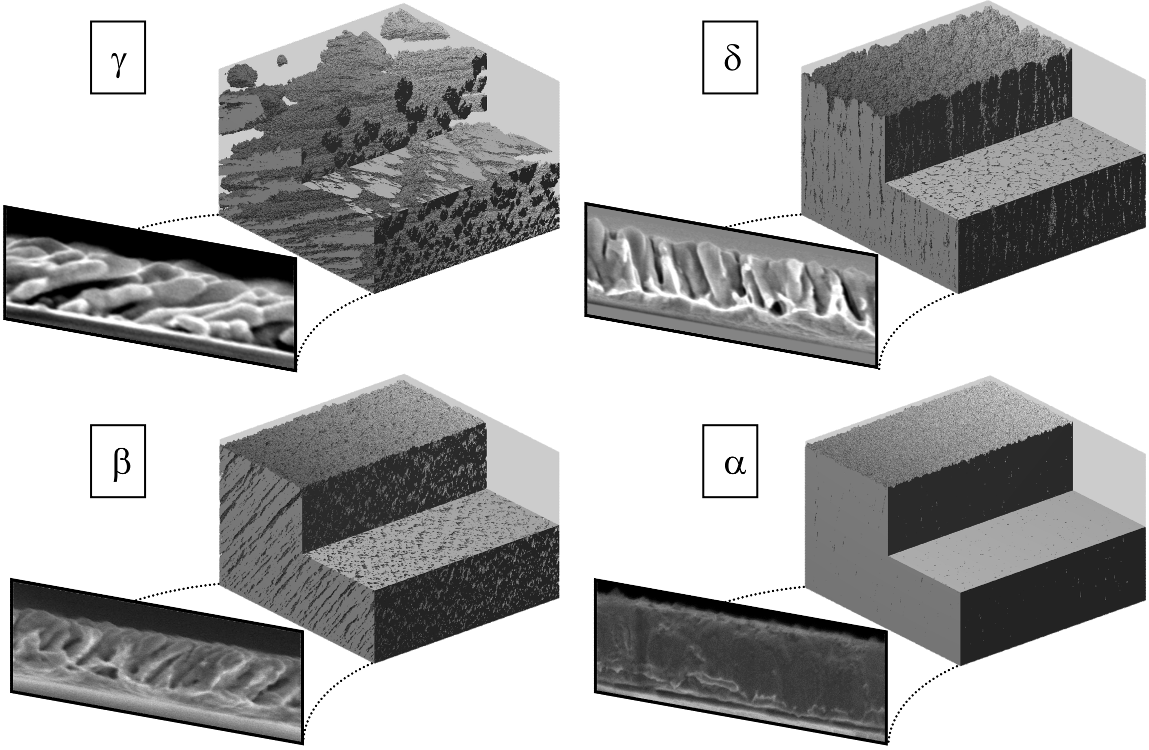

Fig. 1: The four generic nanostructured Au films obtained by magnetron sputtering at oblique incidence. The “cubes” are simulated films whereas the cross-sections are FESEM images of real samples.

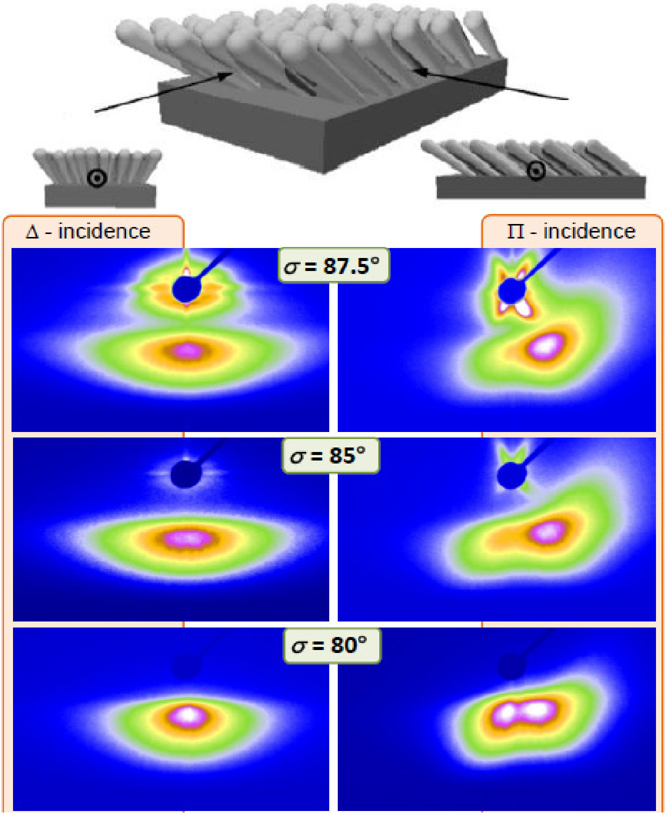

Fig. 2: GISAXS spectra of γ-type films for Δ and Π incidence: the asymmetric patterns in the latter case indicate the existence of tilted individual nanocolumns.