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Thin films composed of gold nanoparticles dispersed in a dielectric matrix: The influence of the host matrix on the optical and mechanical responses

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ABSTRACT

Gold nanoparticles were dispersed in two different dielectric matrices, TiO_2 and Al_2O_3, using magnetron sputtering and a post-deposition annealing treatment. The main goal of the present work was to study how the two different host dielectric matrices, and the resulting microstructure evolution (including both the nanoparticles and the host matrix itself) promoted by thermal annealing, influenced the physical properties of the films. In particular, the structure and morphology of the nanocomposites were correlated with the optical response of the thin films, namely their localized surface plasmon resonance (LSPR) characteristics. Furthermore, and in order to scan the future application of the two thin film system in different types of sensors (namely biological ones), their functional behaviour (hardness and Young's modulus change) was also evaluated. Despite the similar Au concentrations in both matrices (~11 at.%), very different microstructural features were observed, which were found to depend strongly on the annealing temperature. The main structural differences included: (i) the early crystallization of the TiO_2 host matrix, while the Al_2O_3 one remained amorphous up to 800 °C; (ii) different grain size evolution behaviours with the annealing temperature, namely an almost linear increase for the Au:TiO_2 system (from 3 to 11 nm), and the approximately constant values observed in the Au:Al_2O_3 system (4–5 nm). The results from the nanoparticle size distributions were also found to be quite sensitive to the surrounding matrix, suggesting different mechanisms for the nanoparticle growth (particle migration and coalescence dominating in TiO_2 and Ostwald ripening in Al_2O_3). These different clustering behaviours induced different transmittance-LSPR responses and a good mechanical stability, which opens the possibility for future use of these nanocomposite thin film systems in some envisaged applications (e.g. LSPR-biosensors).

1. Introduction

Noble metal particle powders have been used for many centuries, providing wonderful optical effects in Roman glasses or in the windows of medieval cathedrals. In the past few years, plasmonic nanoparticles (NPs) such as Au have been intensely investigated since they present unique electronic and optical properties [1–8]. The importance of these materials relies on the localized surface plasmon resonance (LSPR) phenomenon, which results from charge density oscillations confined to metallic nanoparticles, which can give rise to (i) strong absorption bands, (ii) the enhancement of the electromagnetic field near the nanoparticles and (iii) the scattering to the far field [9–12]. Furthermore, the physical response of the noble metal nanoparticles can be tailored from their geometric characteristics (size, shape and distribution) and surrounding dielectric environment and hence present tuneable LSPR-band characteristics within the visible range of the electromagnetic spectrum [11–18]. For that reason, they are considered to be useful for a wide range of technological applications, including plasmon-based detectors and modulators [19], LSP-enhanced solar cells [20] and light emitting diodes [21], as well as in plasmonic sensing such as the case of the detection of molecules (e.g. SERS) and biological agents (e.g. optical biosensors) [22–29]. Another field where metal NPs are being widely used is heterogeneous catalysis, where the host oxide

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matrix plays an important role since it controls the mechanisms of particle growth and aggregation [30–33]. For example, in some cases the catalytic activity of NPs (e.g. Au) decreases when they grow in size from 2–3 nm to 7–10 nm [31].

In recent works, it was demonstrated that magnetron sputtered thin films from a Ti–Au target, followed by an appropriate post-deposition heat-treatment, is a convenient way to produce ensembles of Au nanoparticles embedded in a TiO_2 matrix, with characteristic LSPR absorption bands [7,18,34]. The magnetron sputtering technique has been widely used since it is associated to low cost production, being relatively simple and versatile in comparison to traditional preparation methods (colloidal solutions, lithography, laser ablation, electrodeposition, etc.) [9,35]. It has been reported that the size, shape and distribution of the nanoparticles throughout the matrix are particularly important for the LSPR intensity and broadening, while the dielectric function of the host matrix influences the LSPR peak position [11,18,33,36].

In order to study the influence of the dielectric environment on the LSPR characteristics of gold nanoparticles, two distinct dielectric matrices were selected, Al_2O_3 and TiO_2. These matrices were selected since they present very different refractive indexes and due to their particular characteristics and properties [33]. Al_2O_3 is an insulating material, which is widely used in optical and mechanical applications due to its excellent corrosion resistance, good mechanical strength and high hardness; as well as high transparency [37] and low refractive index (about 1.7) [38]. Actually, Al_2O_3 is also an excellent material for sensing [39]. On the other hand, TiO_2 is a semiconductor material (bandgap: 3.0 to 3.4 eV) [40], known for its biocompatibility, non-toxicity, chemical stability, high hardness and high optical transmittance, combined with a high refractive index, ranging between 2.0–2.2 for amorphous, up to 2.6 for anatase or even up to 2.9 for rutile [41–44]. Due to these characteristics, TiO_2 is widely used in several optical devices, dye-sensitized solar cells, photocatalysis, gas sensors and biomedical applications [45–48].

The nanocomposite films were deposited by magnetron sputtering using Au pellets encrusted on pure Ti and Al targets, and then subjected to a standard annealing treatment in air atmosphere. The number of pellets was optimized in order to produce two sets of films, Au:Al_2O_3 and Au:TiO_2, with similar Au concentrations in the matrix. The microstructure (structure, morphology, grain size and size distribution) of the films was studied as a function of the annealing temperature and it was correlated with the optical behaviour of the films. Furthermore, and taking into account the possibilities of application of these thin film systems in biological sensor devices, the characterization of some functional properties will deserve a particular emphasis. In this sense, hardness and Young's modulus of the films were also studied and correlated with both structural and morphological features. It is widely known and accepted that these two properties are crucial for any given thin film system, namely because of the mechanical resistance that is always required, but above all in terms of elasticity behaviour, which is of major importance if a polymeric-based substrate might be targeted, as in the present case.

2. Experimental details

Reactive DC magnetron sputtering deposition was used to deposit thin films composed of Au atoms/clusters embedded in two different host matrices: aluminium oxide (Al_2O_3) and titanium oxide (TiO_2). In order to produce the Au:TiO_2 films, a pure Ti target (200 × 100 × 6 mm^3, 99.8% purity), with Au pellets placed on its preferential erosion zone, was sputtered in an Ar/O_2 plasma. The films were prepared using a gas atmosphere composed of Ar (partial pressure of 0.40 Pa) and O_2 (partial pressure of 0.056 Pa). The working pressure (about 0.45 Pa) was constant during the deposition of the films. The oxygen partial pressure was chosen according to the hysteresis experiment, which is described in more detail in Ref. [7], in order to guarantee the formation of a close-stoichiometric TiO_2 matrix. A DC current density of 100 $A \cdot m^{-2}$ was applied in the Ti–Au target. In order to obtain the Au:Al_2O_3 films, a similar procedure was used. Au pellets were placed in an Al target (200 × 100 × 6 mm^3, 99.96% purity) and the cathode was also sputtered using an Ar/O_2 atmosphere. However, in order to have a stable discharge, the current density applied to the Al–Au target was 75 $A \cdot m^{-2}$ and the Ar partial pressure increased to 0.45 Pa. The O_2 partial pressure was adjusted to 0.054 Pa according to the hysteresis experiment, performed also to the Al target. The working pressure was 0.50 Pa. Furthermore, no arcs were detected during deposition of Au:Al_2O_3 films, probably due to the presence of the Au in the Al target. For each system, Au:TiO_2 and Au:Al_2O_3, several sets of films were deposited using different numbers of Au pellets, varying from 1 to 10 [7] and from 1 to 6, respectively. From the whole series of samples, two sets of films, one of Au:TiO_2 and another of Au:Al_2O_3, were selected for this study based on their properties and chemical composition (similar Au concentration). Table 1 summarizes the deposition conditions of the 2 sets of studied samples.

Glass lamellae ISO 8037 (for the optical characterization) and silicon (100) (for chemical, structural, morphological and mechanical analysis) were selected as thin film substrates. A rotating sample holder was used, positioned at 70 mm from the target, rotating at a constant speed of 9 rpm, heated at 100 °C before discharge ignition. The substrate temperature during deposition was estimated by a resistance temperature detector (RTD), model Pt100 (JUMO Instruments Co. Ltd.), placed in the back of a Si substrate [49]. However, this measurement was performed in static mode and before the films deposition. After 10–15 min. The substrate temperature was nearly constant, at about 200 °C for the TiO_2 and 160 °C for Al_2O_3.

After the deposition of the films, the samples were subjected to an in-air heat-treatment. The annealing experiments were conducted in a furnace at atmospheric pressure, using a temperature range from 200 to 800 °C. The heating ramp was set to be 5 °C/min until the desired temperature was attained. The isothermal period was fixed in 60 min. The samples were let to cool down freely before their removal from the furnace.

The chemical composition of the films was analysed by Rutherford Backscattering Spectrometry (RBS). RBS measurements were carried out using a 2 MeV ^4He beam at an angle of incidence 0°. There were three detectors in the chamber: a standard one at 140°, and two pin-diode detectors located symmetrical to each other, both at 165° (detector 3 on same side as standard detector 2). The RBS profiles were analysed with the IBA DataFurnace NDF v9.6a [50–52].

The evolution of the crystalline structure as a function of the annealing temperature was studied by X-ray diffraction in situ during annealing (in situ XRD). The equipment used was a θ–θ Brucker D8 Advance System diffractometer, with a Cu-Kα radiation, in a Bragg–Brentano configuration, equipped with a furnace. The same annealing procedure described above was applied. By using the WinFit software, the Au nanoparticle size was estimated by fitting the diffraction peaks with a Pearson VII function, and using the integral breadth method.

Table 1
Deposition condition of the as-deposited films.

Conditions	Au:TiO_2	Au:Al_2O_3
Ar flow, partial pressure	60 sccm, 0.40 Pa	70 sccm, 0.45 Pa
O_2 flow, partial pressure	7 sccm, 0.056 Pa	6.75 sccm, 0.054 Pa
Total pressure	0.50 Pa	0.55 Pa
No. Au pellets, total area	3, 27 mm^2	4, 36 mm^2
Relative Au pellets area	0.14%	0.18%
Current density	100 $A \cdot m^{-2}$	75 $A \cdot m^{-2}$
Target potential	470 V	290 V
Deposition time	5400 s	7200 s
Thickness	0.40 μm	0.30 μm
Deposition rate	4.4 $nm \cdot min^{-1}$	2.5 $nm \cdot min^{-1}$
Bias	Grounded	Grounded