Silver and gold nanoparticles in nanometric confined templates: synthesis and alloying within the anisotropic pores of Oblique Angle Deposited films

Julian Parra-Barranco, Juan Ramon Sanchez-Valencia, Angel Barranco, Agustín R. González-Elipe**

Dr. J. Parra-Barranco, Dr. J. R. Sanchez-Valencia, Dr. A. Barranco, Prof. A.R. González Elipe.

Nanotechnology on Surfaces Laboratory, ICMS, Materials Science Institute of Seville (CSIC-US). C/ Americo Vespucio 49, 41092, Seville (Spain)

Corresponding Authors

J.R. Sanchez-Valencia * E-mail: jrsanchez@icmse.csic.es

A.R. Gonzalez-Elipe * E-mail: arge@icmse.csic.es

Supplementary material for this article is available online

KEYWORDS. Nanotemplates, Surface Plasmon Resonance, Anisotropic metal nanoparticles; Oblique and Glancing Angle Deposition (OAD and GLAD), Porous thin films, Laser annealing.

Abstract

In this work we have developed an infiltration methodology to incorporate metal nanoparticles (NPs) with controlled size and shapes into the open voids available in Oblique Angle Deposited (OAD) thin films. These NPs exhibited well-defined surface plasmon resonances (SPR). The nanometric confined space provided by their porous microstructure has been used as a template for the growth of anisotropic NPs with interesting surface plasmon resonance properties. The fabrication methodology has been applied for the preparation of films with embedded silver and gold NPs with two associated plasmon resonance features that developed a dichroic behaviour when examined with linearly polarized light. A confined alloying process was induced by near IR nanosecond laser irradiation yielding bimetallic NPs with SPR features covering a large zone of the electromagnetic spectrum. The possibilities of the method for the tailored fabrication of a wide range colour palette based on SPR features are highlighted.

1. Introduction

During the last decades, metal nanoparticles (NPs) or assemblies with controlled composition, geometry, size and surface state have deserved a continuous interest due to their outstanding physical (e.g., optical or magnetic) and chemical (e.g. catalytic) properties.[1–5] These morphological features have been controlled using a large variety of chemical processes in liquid phase.[6–10] However, wet methodologies usually face the inconvenient that the synthesized NPs may aggregate by van der Waals forces, a feature that hinders applications associated to the physical properties of single and isolated entities.[11] To overcome this problem, alternative procedures entailing NPs synthesis and immobilization on solid supports have been developed,[12–14] where generally a random and un-oriented distribution of isolated particles is obtained.

Controlling the aspect ratio of anisotropic noble metal NPs is critical to tune their Surface Plasmon Resonance (SPR) bands and dichroic behaviour when examined with linearly polarized light.[14–20] SPR features are the result of a collective oscillation of the free electrons at the metal surfaces that produces a localized absorption of light and an important electromagnetic field enhancement in the proximities of NPs.[21,22] Due to this surface-related character, SPR bands are affected by the nature, size, shape and dielectric environment around the metal nanostructures.[4,23–25] In particular, anisotropic metal NPs or other plasmon resonance nanostructures showed different SPR modes depending on the relative orientation of the incident light electric-field along their long (longitudinal mode, LSPR) or short (transverse mode, TSPR) axes. Relying on this characteristic, their optical response has been used for the fabrication of dichroic filters, polarized light nanosources and encoding data systems, among other applications.[16,26–29] A general condition for the functionality of these systems is that the individual nanostructural features incorporated into the device present a common orientation along a preferential axis. In the case of NPs this has been achieved by means of hosts or templates with anisotropic pores of similar size defining a preferential orientation.[14] Synthesis procedures relying on this approach use the template voids as nanoreactors to grow NPs in their interior. Advantages of such a methodology include: 1) the use of green solvents and reactants since shape is not controlled by organic surfactants but defined by the template,[13,30] 2) natural inhibition of nanoparticle aggregation[31] and 3) fabrication of highly aligned anisotropic structures.[16,26] Liquid and suspension procedures consisting in the alloying or merging of two metals in a single structure (e.g., core shell structures or alloyed

NPs[32,33]) have been attempted to expand the optical response ranges. However, only single metal NPs (e.g., silver or gold) have been synthesized within template structures.

Oblique angle deposited (OAD) thin films prepared by evaporation present a nanostructure formed by highly aligned tilted nano-columns[34–38]. This microstructural feature bestows the OAD samples with anisotropic optical properties which, in the case of noble metals, have been used for developing photonic components such as coloured dichroic polarizers or SERS based sensors.[39–41] Unfortunately, Oblique Angle Deposition consumes a high amount of metal due to the high substrate-source distance (to ensure a narrow angular distribution) and to the tilting angle of the substrates (the flux of condensing molecules/atoms is reduced by the cosine of the deposition angle). These factors, together with the high electrical consumption required to electron evaporate metals with high thermal conductivity (e.g., Ag, Au), makes that direct OAD deposition of metals is not always suitable for mass applications.

A remarkable characteristic of OAD thin films is that, depending on the material and deposition angle, their nanocolumns arrange in the form of “bundles” aligned along the direction perpendicular to the incoming material flux.[34,38,42] The size of these anisotropic pores separating the bundles depends on the type of material and film deposition angle.[34,38] We have shown in previous works that this bundling association in transparent films deposited by OAD induces an anisotropic growth of metal nanoparticles upon incorporation in the film pores either by vacuum or wet methodologies.[16,17,26,36,43] This template-based approximation makes use of much less noble metals than procedures based on their direct OAD.

In the present work, we have developed a template method for the synthesis of both Ag and Au NPs within the anisotropic pores of SiO₂ thin films prepared by OAD. Primarily, we show that the pore space of the OAD thin films may act as a nanometric template to tailor the growth of metal NPs of controlled size. In addition, we show that the anisotropy of the void space defined by the nanocolumnar bundles existing in the SiO₂ thin films induces the growth of oriented disc-shape Au NPs. Finally, the use of the pore space as a nanoreactor is proved upon Near Infrared (NIR) laser annealing of bimetallic composite films in a process that yields size-controlled alloyed Ag:Au NPs embedded in the films. This work is the continuation of a previous investigation showing that anisotropic gold NPs can be synthesized within the tilted mesopore spaces separating the nanocolumns of OAD SiO₂ thin films.[16] Herein we go a step forward showing the possibility of fabricating either two metals and/or alloy NPs inside an OAD oxide thin film acting as template. The reported methodology does not make use of additives to control the size of the nanoparticles and therefore the growth is template directed.

The resulting composites possessed a rich SPR spectral response (i.e., an ample colour pallet associated to the Ag, Au and Ag:Au alloy NPs) and an strong dichroic behaviour associated to the disc-shape of the individual Au NPs. The results reported here represent an important advance in the controlled synthesis of anisotropic metal nanoparticles and alloying processes into OAD film voids. This latter aspect is enabled by the high transparency, inertness and chemical stability of SiO₂ layers. The unique plasmonic properties, surface area, open porosity and biocompatibility of the anisotropic metal nanoparticles synthesized will have a significant impact not only in the field of photonics and selective dichroic systems,[20,44,45] but also in biological applications such as sensing and imaging among others.[14–17,46]

2. Materials and Methods

2.1. Sample preparation.

SiO₂ thin films were prepared in an electron beam evaporator using pellets of this material as target. Quartz plates or pieces of a Si (100) wafer with a size of 2x2 cm² were used as substrates. Deposition was carried out at room temperature in 10⁻⁴ torrs of O₂ (residual pressure in the reactor was 10⁻⁶ torrs). Two types of OAD films were fabricated by placing the substrates at glancing zenithal angles, α , with respect to the evaporator source of 60° and 80° (**see Figure S1, available online**). Such oblique geometries produced films with a tilted columnar microstructure caused by geometrical shadowing during the thin film growth.[34] For SiO₂ these nanocolumns associate in the form of lateral “bundles” or strips along the perpendicular direction to the incoming material flux.[16,37,42] The lateral distance between strips formed along the perpendicular to the evaporation direction increases for the films prepared at larger zenithal evaporation angles. These OAD thin films were used as templates for the chemical synthesis of Ag and Au NPs without mediating any further treatment or conditioning.

For the preparation of silver NPs, Ag⁺ cations were infiltrated in the films voids using a solution of PMMA (0.5% (w/v) and AgClO₄ (60 mM) in acetone which was spin coated and dried onto the porous SiO₂ OAD layers. The obtained samples were then heated up to 270 °C with a 5° C/min ramp under a constant flux of a mixture H₂:Ar (5% H₂) at 1 atm. This thermal treatment at a temperature above the PMMA glass transition temperature (100-160°C) promotes the polymer and AgClO₄ diffusion into the SiO₂ pores. In other words, the PMMA is used as a sweep vector of silver cations in a kind of Melt Capillary Infiltration method.[16] In addition, the Ar:H₂ atmosphere produced the complete reduction of silver inside the pores and the formation

of silver NPs in the film voids. Some excess of PMMA and silver precursor at the surface were removed by ultrasonic treatment in acetone during 15 minutes. A small amount of PMMA was deliberately left inside the voids to assist the posterior reduction of gold precursor. To this aim, before proceeding to gold NP formation, the presence of a little fraction of polymer remaining into the voids of the Ag/SiO₂ thin films was confirmed by FT-IR reflectance measurements (see **Figure S2**). Gold was incorporated into these Ag/SiO₂ thin films by immersion in a solution of AuClO₄ (120 Mm) during different periods of time, 10, 20, 30 min. In this step, gold precursor reduction and NP formation was induced by the residual PMMA still present in the pores and a minority redox reaction with the silver NPs grown in the first step.[16] The formation of silver and gold NPs in the SiO₂ template films (i.e., Ag:Ag/SiO₂) was ascertained by the UV-Vis recording of SPR spectra.

Laser annealing to induce the alloying of the silver and gold NPs formed inside the films was performed at room temperature with a 20 W diode-pumped Nd:YAG (Powerline E, Rofin-Baasel Inc.) unpolarized laser emitting at 1064 nm with 100 ns of pulse width and a 20 kHz repetition rate.[26] The films were scanned with a spot of 0.1 mm diameter at a speed of 1 m s⁻¹. The laser power used for the treatments will be referred as a percentage of its maximum irradiance, $P_{MAX} = MLP = 240 \text{ kW/cm}^2$.

The nomenclature used for the samples is (Metal) / (OAD film) where: (Metal) is Ag or Au depending on the metal incorporated, or Ag:Ag if the layer contains the two metals; Ag-Au refers to alloyed NP films; (OAD film) is 60° or 80°, indicating the zenithal angle used for the deposition of the SiO₂ layers.

2.2. Characterization methods

The microstructure of the films deposited on a silicon wafer was examined by Field Emission Scanning Electron Microscopy (FESEM) in a Hitachi S5200 microscope operated at 2KV in backscattered detection mode. The backscattered electron image is sensitive to heavier elements thus allowing a better visualization of the Ag and Au NPs. Cross sectional views were obtained by cleaving the silicon substrates. Samples were cleaved along two perpendicular directions to cross section viewing the films along the bundling directions and its perpendicular. This allows a direct observation of, possibly, dissimilar x-z and y-z planes of the films (see Figure 1 a-c).

The Electron Microscope system is equipped with a Scanning Transmission Electron Detector (noted as STEM measurements) that was used to analyse individual particles and with energy dispersive X-ray spectrometer (EDX) to perform their elemental analysis.

The optical properties of the films were studied by transmittance (beam impinging at normal incidence) and specular reflectance (at 30°) measurements in a Cary 100 UV-Vis spectrophotometer (VARIAN) in the 300-800 nm range and a 1 nm monochromatic step. The monochromatic incident beam used for the analysis was either unpolarised or linearly polarized along two different directions, x and y, according to the coordinate axis in Figure 1 b). CIELab color space coordinates for both x- and y- polarizations were calculated from the transmittance spectrum by using a D65 illuminant.[47]

Real photographs of some representative samples have been taken by placing the samples on top of a white light screen and using a single linear polarizer to observe their anisotropic optical response.

Specular Reflectance Fourier Transformed Infrared (FT-IR) spectroscopy was analysed in a Bruker IFS 66/S spectrometer. For this type of measurements, the OAD samples were deposited onto a 100 nm gold thin film deposited on a silicon wafer with a Ti interlayer, acquired from Sigma-Aldrich.

3. Results and discussion

The OAD SiO₂ thin films were used in first place to synthesize silver NPs inside their inter-bundles voids, using the experimental methodology detailed in the experimental section.[16] It is noteworthy that SiO₂ is an insulator material and becomes charged under the electron beam impingement during the SEM measurements shown in the Figure 1. This effect is the responsible of the slightly blurry appearance of the images. Figures 1 d) and e) present two perpendicular cross sectional SEM images of the Ag/60° composite thin films along the y-z and x-z planes, respectively. As schematized in Figure 1 a), c), these two images clearly reveal the tilted columnar nanostructure of the template thin films but no significant differences in silver particle size along the two observation directions, likely indicating that the silver NPs, with diameters between 20-50 nm, have a rather spherical shape. In addition, the optically isotropic behaviour of the silver NPs determined with polarized light (see next section) further confirmed their quasi-spherical shape. This spherical shape is tentatively attributed to the high mobility of silver at the relatively high temperature used for their synthesis.

Secondly, gold NPs were grown inside the voids of the SiO_2 template films already containing silver NPs. For this aim, the remaining PMMA initially utilized as sweep vector for Ag infiltration acted as a reducing agent to synthesize the gold NPs and as a protective barrier separating Ag and Au NPs to avoid their mixing or the formation of core-shell structures (the separate formation of NPs of these two metals was proved by EDX measurements **(Figure S3)**).

Figures 1 f-g) (Ag:Au/60°) and h-i) (Ag:Au/80°) show orthogonal cross section views of these two samples along the y-z and x-z planes. It is apparent in the images that the density of particles in these bimetallic samples has increased with respect to the monometallic case. In addition, in sample Ag:Au/60° some NPs appeared elongated along the y-z plane (Figure 1f), a feature that, to a minor extent, was also apparent in sample Ag:Au/80° where particles presented a larger size (Figure 1h). We relate this anisotropic growth in the form of discs to the confinement of NPs between the bundle walls.

Figure 1. a-c) Scheme of cross section views of the NPs distribution inside the SiO₂ films along the y-z (a), x-y (b) and x-z (c) planes. The two perpendicular planes used to cleave the samples for their cross sectional analysis by SEM are the y-z (a, left) and x-z (c, right). The formation of anisotropic NPs (brown color) between bundled walls (blue forms) is described in the schemes and experimentally observed for gold NPs in sample Ag:Au/60°. d), f), h) Cross sectional images along the y-z plane of Ag/60° (d), Ag:Au/60° (f) and Ag:Au/80° (h). e), g), i) Cross sectional images of the same samples along the x-z plane

The growth of gold discs in sample Ag:Au/60° can be easily understood in terms of the Scheme 1. Spherical Au NPs start growing until they touch the adjacent bundle walls confining the space where they are growing. From this point, the NPs are forced to grow in the free directions available in the voids and to develop their characteristic disc-shape. It will be shown that these Au NPs present quite different longitudinal (L) and transversal (T) SPR spectral

modes which, together with their common alignment along a given direction (determined by the nanocolumnar bundles) produces a strong dichroism for the composite films (see below).

Scheme 1. Template synthesis of disc-shape gold NPs. The initially spherical growth regime is followed by the disc growth once the particle size exceeds the distance between bundle walls.

The plasmonic behaviour of the composite thin films has been characterized by UV-Visible transmittance measurements analysed with x- and y-polarized light. Spectra are presented in **Figure 2** for samples Ag/60° (a) and Ag/80° (e) and bimetallic samples Ag:Au/60° (a-d) and Ag:Au/80° (e-h). According to these spectra, silver NPs present a very weak optical anisotropy since the films showed similar SPR bands with slightly different intensities and centred at 393 and 396 nm when recorded with x- and y-polarized light, respectively. These absorption maxima and the symmetrical shape of the bands are consistent with the presence of quasi-spherical particles with a relatively narrow size distribution around 20-50 nm [48] as observed in the SEM images in Figure 1 d), e).

The growth of Au NPs was conducted by dipping the OAD films containing silver NPs for increasing times in a solution containing AuClO_4 (see Experimental section). The x- and y-polarized spectra of Ag:Au/60° and 80° samples are shown in Figure 2 b)-d) and f)-h), respectively. These spectra exhibited two plasmon features, the first attributed to silver NPs (at around 400 nm) and the second to gold NPs (at 500-600 nm). It is noteworthy that the SPR at 400 nm remained unaltered after the incorporation of Au NPs. This discards the formation of alloys or core-shell structures which are typically accompanied by important changes in the SPR bands.[33] The SPR associated to Au NPs presented a high optical anisotropy when examining the samples with polarized light along the x- (blue) and y-directions (red). We attribute these two

different light absorptions to the longitudinal (with x-pol) and transversal (with y-pol) SPR modes of the disc-shape of the Au NPs. Figure 2 b-d) and f-h) reveal an increasing difference in the wavelength and intensity of these two SPR modes as the gold incorporation time increased up to a maximum of 30 min. For sample Ag:Au/60° (Figure 2 b-d), the increased separation between bands resulted from a progressive shift of the LSPR (x-pol) mode from 560 to 605 nm (see blue dashed line), whereas the TSPR (y-pol) remaining unchanged at approximately 510 nm. A similar, though less pronounced effect, was observed for sample Ag:Au/80°, where the LSPR only shifted from 550 to 560 nm for 10 to 30 min of processing time. In an attempt to have a fuller picture of the optical properties, specular reflectance spectra of the sample Ag:Au/60° were recorded at 30° (red curves) with unpolarised light (see **Figure S4** in the supporting information). The typical oscillations due to the refractive index contrast air/OAD film/glass were enhanced in these reflectance measurements which, together with the polarization induced refraction/reflection effects under non-normal angles, hampered a precise evaluation of the SPR peaks.

As it can be observed in Figure 2, the SPR bands are wide indicating a relatively large size distribution of the Ag and Au nanoparticles. This is likely the result of the heterogeneous character of the SiO₂ nanocolumnar template and of a synthesis method that does not make use of chemical additives to control the size of the nanoparticles. Although it is not the scope of this work, we envisage that the growth process can be highly improved by using chemical methodologies to control nanoparticle growth.[10,19] The template growth model shown in the scheme 1 is consistent with the smaller optical anisotropy observed for sample Ag:Au/80°, where the separation between bundles along the y axis is larger than in the 60° SiO₂ sample (see Figure 1). This increased separation between bundles can be seen in **Figure S5** showing high resolution cross section SEM images of 60° (a) and 80° (b) OAD SiO₂ samples. The photographs taken with x- and y-polarizers for samples Ag/60° and Ag:Au/60°(30 min) permit a direct visualization of sample colours: a yellow-green colour with very small or negligible differences was found for samples Ag/60°, while for sample Ag:Au/60°(30 min) blue and pink colours were observed depending on polarizer orientation.

Figure 2. UV-Vis Transmittance spectra recorded with x- and y-polarized light for Ag:Ag/Au/60° (a-d) and Ag:Ag/Au/80° (e-h) samples. a)-d) Series of spectra of sample Ag:Ag/Au/60° before the immersion in the AuClO_4 solution (a), and after the immersion for 10min (b), 20 min (c) and 30 min (d). e)-h) The same series of spectra are reported for metallic samples prepared in SiO_2 80° host thin films. The plots show vertical lines to guide the eye in the spectral positions of the different SPR modes observed. a) and d) include photographs of the corresponding samples taken with x- and y- oriented polarizers. The xyz axes defined with respect to the samples surface as indicated in the photographs have been also included.

In previous works we have demonstrated that laser annealing of OAD- SiO_2 samples containing either silver or gold nanoparticles can be used to modify their geometry and therefore the optical properties associated to the plasmon bands.[16,26] Herein we have used the

confined space provided by the OAD SiO₂ thin films to control the laser alloying processes between different metal NPs embedded in their voids. First, we have studied the effect on Ag/60° samples irradiated with an infrared nanosecond laser at different powers. Figure 3 shows the optical evolution of laser treated Ag/60° film at 50 and 90% maximum laser power (MLP). In all cases, laser annealing produced a slight blue shift in the plasmon absorption band, their narrowing and an increase in intensity. These optical modifications rendered a yellow colour for the samples (see Figure 3 d) and were more significant at higher laser powers. They can be understood as resulting from the weld fragmentation of bigger particles and their resize into smaller ones. It is also striking that low power laser treatments (30 % MLP) did not produce any significant optical change, thus suggesting the existence of a threshold laser power to induce the fragmentation of particles.

Figure 3. UV-Vis Transmittance spectra recorded with x- and y-polarized light for sample Ag/60° as prepared (a) and laser treated at 50% (b) and 90% (c) of maximum power (MLP=240 kW cm⁻²). d) Photographs of the samples illuminated with y-(top) and x-polarized (bottom) visible light. The photographs show four areas treated with 30, 50, 70 and 90% MLP.

The optical changes induced by laser treatment were radically different in the bimetallic samples. Figure 4 shows the evolution of the SPR spectra of sample Ag-Au/60° treated at 50 and 90% MLP. For the sake of comparison, spectra of sample Au/60° subjected to similar laser treatments are plotted in Figures 4 a-c) with dashed lines.[16] The laser treatment of sample Ag-Au/60° produces a gradual loss of the gold associated SPR band anisotropy and the progressive vanish of the silver SPR band (originally at 400 nm). As a result, the 90% MLP laser treated Ag-Au/60° sample developed a single broad absorption band at 500 nm with almost no optical anisotropy. We attribute this merging of the gold and silver SPR modes to the formation of bimetallic alloy spherical nanoparticles, although a direct observation of the laser induced structural changes of nanoparticles was not possible due to the insulating nature of the glass substrates that hinders their visualization by electron microscopy.

Figure 4. UV-Vis Transmittance spectra recorded with x- and y-polarized light for sample Ag:Au/60°(0%) as prepared (a) and treated with a laser at 50% (b) and 90% (c) MLP. Equivalent spectra recorded for sample Au/60° plotted with dashed lines are shown for comparison. d) Photographs of the samples illuminated with y- and x-polarized visible light showing the two areas treated with laser at 50 and 90% MLP. e) Scheme of the alloying process taking place during the laser treatment.

In previous works,[16,26] we have demonstrated that nanosecond-laser treatments with pulse durations longer than the metal electron-phonon relaxation time produce nanoparticle reshaping due to heat accumulation in the metal. In the bimetallic films studied here reshaping is complemented with the alloying of silver and gold. A model of the bimetallic alloy formation and spherical reshaping by laser treatment is shown in Figure 4 e), assuming that silver and gold clusters are close enough to enable their intermixing without entailing a long diffusion length for the atoms. Gold-silver alloy formation is thermodynamically favoured by a negative mixing enthalpy, [32,33,49] which ensures the stability of the formed Ag:Au NPs. This metal alloying was accompanied by a slight damage of the SiO₂ template films as evidenced by an increase in light scattering at low wavelengths observed in the reflectance spectra (see **Figure S4 b**).

Alloying produces significant differences when the samples were observed with the bare eyes. The photographs in Figure 4 d) taken with x-and y-oriented polarizers show a gradual loss in anisotropy as the laser power increased to 90% MLP when a similar pink colour was obtained for the two polarizers. It is noteworthy the excellent optical contrast between the non-treated and laser treated areas, a feature that in previous works was utilized for optical encoding.[16,26]

The rich variety of colours achievable by NPs synthesis in the template structure of OAD thin films is illustrated in a CIELAB colour space representation in Figure 5. CIELAB colour coordinates have been calculated from the transmittance spectra in Figures 2 d), 3 a), c) and 4 a), c) for both x- and y-polarizations. Figure 5 shows the bimetallic Ag:Au/60° and monometallic Ag/ and Au/60° systems before and after the 90% MLP laser treatment. CIELAB colour space is well-suited to highlight colour differences, since the luminosity (L*) is taken as a separate coordinate.[47,50] In this representation, coordinates a* and b* represent the green-red and yellow-blue colours, respectively and the origin (a*=b*=0) indicates the absence of colour. According to the plot in Figure 5, the laser annealed Ag/60° samples change their colour to a stronger yellow, characterized by the a* coordinate close to zero, and a very high b* value. In contrast, the Au/60° sample, characterized by an initial dichroic response (note the two separate coordinates in the diagram) experienced a small modification in colour coordinates upon laser irradiation (slight colour alteration resulted from the merging of the coordinates associated to the loss of optical anisotropy). Also, samples Ag:Au/60° were originally characterized by two points in the diagram and rendered a single point after laser alloying (see the red arrow highlighting the coordinate changes upon laser irradiation). The initial dichroic response of this sample rendered a more saturated red colour upon laser annealing. The quite different colour coordinates

represented in this diagram confirms the variety of colours achievable, varying from blue to pink-orange that can be obtained with the template synthesis approach described in this work. It is noteworthy that despite the rich variety of plasmonic colours and dichroism obtained in this work, it is less rich than that achievable with more sophisticated methodologies such as electron or nanoimprint lithography,[51,52] yet the simplicity and versatility of the OAD template plus laser methodology is a very promising plus for future developments in photonics.

Figure 5. CIELAB color coordinates a^* and b^* extracted from the x- (black square) and y-polarized (grey circle) UV-Vis transmittance spectra of the samples Ag/60°(90%MLP), Au/60°(90%MLP) and Ag:Au/60°(90%MLP). A photograph of each sample has been included.

4. Conclusions

In this work we have developed a new template methodology to control metal NPs growth and alloying processes in anisotropic confined spaces provided by the pores of OAD columnar thin films. It has been demonstrated that the tilted columnar morphology of OAD films and their association along columns bundles act as a “mold” to restrict the growth of silver and gold NPs in their interior. Another outstanding result is that this template approach can be extended for the synthesis of bimetallic composite thin films and that their laser irradiation induces the formation of alloyed NPs with a size range defined by the void structure of the host SiO₂ thin films. These modifications are gradual and can be tuned with the laser power. The NPs synthesized within the SiO₂ thin films give rise to a large variety of SPR absorption spectra, and

a dichroic behaviour for the samples containing gold prior to the laser treatment. It has been demonstrated that the use of OAD SiO₂ thin films as template for the chemical synthesis of NPs has a general character being a quite versatile procedure for the fabrication of embedded mono, bi- and alloyed NPs, these latter upon laser irradiation. The rich variety of colours and optical properties obtained by this methodology opens the way for the “a la carte” fabrication of advanced optical systems based on SPR.

Author Contributions

A.B. and A.R.G-E initiated and conceived this work. J.P-B fabricated the samples and did the structural and optical characterization with contributions from J.R.S-V. All authors participated in the analysis and interpretation of the results. J.P-B drafted the manuscript with contributions from J.R.S-V and A.R.G-E. A.B. and A.R.G-E coordinated the efforts of the research team. All authors have given approval to the final version of the manuscript.

Acknowledgements

The authors thank the AEI and the Spanish Ministry of Economy and Competitiveness (MAT2013-40852-R, MAT2013-42900-P, MAT2015-6903J-REDC, MAT2016-79866-R, MINECO-CSIC 201560E055 and RECUPERA 2020) and the EU through cohesion fund programs (FEDER) for financial support. JRS-V and AngelB acknowledge funding from EU project *PlasmaPerovSol*. This project has received funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 661480.

References

- [1] Prieto G, Zečević J, Friedrich H, de Jong K P and de Jongh P E 2013 Towards stable catalysts by controlling collective properties of supported metal nanoparticles *Nat. Mater.* **12** 34–9
- [2] Polavarapu L and Liz-Marzán L M 2013 Towards low-cost flexible substrates for nanoplasmonic sensing *Phys. Chem. Chem. Phys.* **15** 5288–300
- [3] Guo S, Zhang S and Sun S 2013 Tuning Nanoparticle Catalysis for the Oxygen Reduction Reaction *Angew. Chem. Int. Ed.* **52** 8526–44

- [4] Kelly K L, Coronado E, Zhao L L and Schatz G C 2003 The Optical Properties of Metal Nanoparticles: The Influence of Size, Shape, and Dielectric Environment *J. Phys. Chem. B* **107** 668–77
- [5] Halas N J, Lal S, Chang W-S, Link S and Nordlander P 2011 Plasmons in Strongly Coupled Metallic Nanostructures *Chem. Rev.* **111** 3913–61
- [6] Samal A K, Polavarapu L, Rodal-Cedeira S, Liz-Marzán L M, Pérez-Juste J and Pastoriza-Santos I 2013 Size Tunable Au@Ag Core–Shell Nanoparticles: Synthesis and Surface-Enhanced Raman Scattering Properties *Langmuir* **29** 15076–82
- [7] Guo S and Wang E 2011 Noble metal nanomaterials: Controllable synthesis and application in fuel cells and analytical sensors *Nano Today* **6** 240–64
- [8] Lohse S E and Murphy C J 2013 The Quest for Shape Control: A History of Gold Nanorod Synthesis *Chem. Mater.* **25** 1250–61
- [9] Dehghan Banadaki A and Kajbafvala A 2014 Recent Advances in Facile Synthesis of Bimetallic Nanostructures: An Overview *J. Nanomater.* **2014** e985948
- [10] Nguyen T-D 2013 From formation mechanisms to synthetic methods toward shape-controlled oxide nanoparticles *Nanoscale* **5** 9455–82
- [11] Pillai Z S and Kamat P V 2004 What Factors Control the Size and Shape of Silver Nanoparticles in the Citrate Ion Reduction Method? *J. Phys. Chem. B* **108** 945–51
- [12] Costa N J S and Rossi L M 2012 Synthesis of supported metal nanoparticle catalysts using ligand assisted methods *Nanoscale* **4** 5826–34
- [13] Sun Y, Mayers B T and Xia Y 2002 Template-Engaged Replacement Reaction: A One-Step Approach to the Large-Scale Synthesis of Metal Nanostructures with Hollow Interiors *Nano Lett.* **2** 481–5
- [14] Paramasivam G, Kayambu N, Rabel A M, Sundramoorthy A K and Sundaramurthy A 2017 Anisotropic noble metal nanoparticles: Synthesis, surface functionalization and applications in biosensing, bioimaging, drug delivery and theranostics *Acta Biomater.* **49** 45–65
- [15] Burrows N D, Vartanian A M, Abadeer N S, Grzincic E M, Jacob L M, Lin W, Li J, Dennison J M, Hinman J G and Murphy C J 2016 Anisotropic Nanoparticles and Anisotropic Surface Chemistry *J. Phys. Chem. Lett.* **7** 632–41
- [16] Gonzalez-García L, Parra-Barranco J, Sanchez-Valencia J R, Ferrer J, Garcia-Gutierrez M-C, Barranco A and Gonzalez-Elipe A R 2013 Tuning Dichroic Plasmon Resonance Modes of Gold Nanoparticles in Optical Thin Films *Adv. Funct. Mater.* **23** 1655–63

- [17] Sánchez-Valencia J R, Toudert J, Borrás A, López-Santos C, Barranco A, Feliu I O and González-Elípe A R 2010 Tunable In-Plane Optical Anisotropy of Ag Nanoparticles Deposited by DC Sputtering onto SiO₂ Nanocolumnar Films *Plasmonics* **5** 241–50
- [18] Camelio S, Babonneau D, Lantiat D, Simonot L and Pailloux F 2009 Anisotropic optical properties of silver nanoparticle arrays on rippled dielectric surfaces produced by low-energy ion erosion *Phys. Rev. B* **80** 155434
- [19] Lohse S E, Burrows N D, Scarabelli L, Liz-Marzán L M and Murphy C J 2014 Anisotropic Noble Metal Nanocrystal Growth: The Role of Halides *Chem. Mater.* **26** 34–43
- [20] Zhu X, Yan W, Levy U, Mortensen N A and Kristensen A 2017 Resonant laser printing of structural colors on high-index dielectric metasurfaces *Sci. Adv.* **3** e1602487
- [21] Sun X and Li H 2016 A Review: Nanofabrication of Surface-Enhanced Raman Spectroscopy (SERS) Substrates *Curr. Nanosci.* **12** 175–83
- [22] Krajczewski J, Kołataj K and Kudelski A 2017 Plasmonic nanoparticles in chemical analysis *RSC Adv.* **7** 17559–76
- [23] Chang W-S, Slaughter L S, Khanal B P, Manna P, Zubarev E R and Link S 2009 One-Dimensional Coupling of Gold Nanoparticle Plasmons in Self-Assembled Ring Superstructures *Nano Lett.* **9** 1152–7
- [24] Murray W A and Barnes W L 2007 Plasmonic Materials *Adv. Mater.* **19** 3771–82
- [25] Noguez C 2007 Surface Plasmons on Metal Nanoparticles: The Influence of Shape and Physical Environment *J. Phys. Chem. C* **111** 3806–19
- [26] Sanchez-Valencia J R, Toudert J, Borrás A, Barranco A, Lahoz R, de la Fuente G F, Frutos F and Gonzalez-Elípe A R 2011 Selective Dichroic Patterning by Nanosecond Laser Treatment of Ag Nanostripes *Adv. Mater.* **23** 848–53
- [27] Zhang Y, Liu Q, Mundoor H, Yuan Y and Smalyukh I I 2015 Metal Nanoparticle Dispersion, Alignment, and Assembly in Nematic Liquid Crystals for Applications in Switchable Plasmonic Color Filters and E-Polarizers *ACS Nano* **9** 3097–108
- [28] Siozios A, Koutsogeorgis D C, Lidorikis E, Dimitrakopoulos G P, Kehagias T, Zoubos H, Komninou P, Cranton W M, Kosmidis C and Patsalas P 2012 Optical Encoding by Plasmon-Based Patterning: Hard and Inorganic Materials Become Photosensitive *Nano Lett.* **12** 259–63
- [29] Kalfagiannis N, Siozios A, Bellas D V, Toliopoulos D, Bowen L, Pliatsikas N, Cranton W M, Kosmidis C, Koutsogeorgis D C, Lidorikis E and Patsalas P 2016 Selective modification of nanoparticle arrays by laser-induced self assembly (MONA-LISA): putting control into bottom-up plasmonic nanostructuring *Nanoscale* **8** 8236–44

- [30] Jin R, Charles Cao Y, Hao E, Métraux G S, Schatz G C and Mirkin C A 2003 Controlling anisotropic nanoparticle growth through plasmon excitation *Nature* **425** 487–90
- [31] Li X and Lenhart J J 2012 Aggregation and Dissolution of Silver Nanoparticles in Natural Surface Water *Environ. Sci. Technol.* **46** 5378–86
- [32] Guisbiers G, Mendoza-Cruz R, Bazán-Díaz L, Velázquez-Salazar J J, Mendoza-Perez R, Robledo-Torres J A, Rodriguez-Lopez J-L, Montejano-Carrizales J M, Whetten R L and José-Yacamán M 2016 Electrum, the Gold–Silver Alloy, from the Bulk Scale to the Nanoscale: Synthesis, Properties, and Segregation Rules *ACS Nano* **10** 188–98
- [33] Qi W H and Lee S T 2010 Phase Stability, Melting, and Alloy Formation of Au–Ag Bimetallic Nanoparticles *J. Phys. Chem. C* **114** 9580–7
- [34] Barranco A, Borrás A, Gonzalez-Elipe A R and Palmero A 2016 Perspectives on oblique angle deposition of thin films: From fundamentals to devices *Prog. Mater. Sci.* **76** 59–153
- [35] Parra-Barranco J, Oliva-Ramirez M, Gonzalez-Garcia L, Alcaire M, Macias-Montero M, Borrás A, Frutos F, Gonzalez-Elipe A R and Barranco A 2014 Bending Induced Self-Organized Switchable Gratings on Polymeric Substrates *ACS Appl. Mater. Interfaces* **6** 11924–31
- [36] Parra-Barranco J, García-García F J, Rico V, Borrás A, López-Santos C, Frutos F, Barranco A and González-Elipe A R 2015 Anisotropic In-Plane Conductivity and Dichroic Gold Plasmon Resonance in Plasma-Assisted ITO Thin Films e-Beam-Evaporated at Oblique Angles *ACS Appl. Mater. Interfaces* **7** 10993–1001
- [37] Sanchez-Valencia J R, Longtin R, Rossell M D and Gröning P 2016 Growth Assisted by Glancing Angle Deposition: A New Technique to Fabricate Highly Porous Anisotropic Thin Films *ACS Appl. Mater. Interfaces* **8** 8686–93
- [38] Hawkeye M M, Taschuk M T and Brett M J 2014 *Glancing angle deposition of thin films: engineering the nanoscale* (Chichester: Wiley)
- [39] Chaney S B, Zhang Z-Y and Zhao Y-P 2006 Anomalous polarized absorbance spectra of aligned Ag nanorod arrays *Appl. Phys. Lett.* **89** 053117
- [40] Liu Y, Fan J, Zhao Y-P, Shanmukh S and Dluhy R A 2006 Angle dependent surface enhanced Raman scattering obtained from a Ag nanorod array substrate *Appl. Phys. Lett.* **89** 173134
- [41] Zhao Y-P, Chaney S B and Zhang Z-Y 2006 Absorbance spectra of aligned Ag nanorod arrays prepared by oblique angle deposition *J. Appl. Phys.* **100** 063527
- [42] Oliva-Ramirez M, Barranco A, Löffler M, Yubero F and González-Elipe A R 2016 Optofluidic Modulation of Self-Associated Nanostructural Units Forming Planar Bragg Microcavities *ACS Nano* **10** 1256–64

- [43] Parra-Barranco J, Sanchez-Valencia J R, Aparicio F J, Garcia-Garcia F, Ferrer F J, Rico V, Lopez-Santos C, Borrás A, Gonzalez-Elise A R and Barranco A 2017 (Invited) Plasma Assisted Oblique Angle Deposition of Transparent and Conductive in-Plane Anisotropic ITO Thin Films *ECS Trans.* **77** 9–15
- [44] Kalfagiannis N, Karagiannidis P G, Pitsalidis C, Panagiotopoulos N T, Gravalidis C, Kassavetis S, Patsalas P and Logothetidis S 2012 Plasmonic silver nanoparticles for improved organic solar cells *Sol. Energy Mater. Sol. Cells* **104** 165–74
- [45] Zhu X, Vannahme C, Højlund-Nielsen E, Mortensen N A and Kristensen A 2015 Plasmonic colour laser printing *Nat. Nanotechnol.* **11** 325–9
- [46] Yang X, Yang M, Pang B, Vara M and Xia Y 2015 Gold Nanomaterials at Work in Biomedicine *Chem. Rev.* **115** 10410–88
- [47] Schanda J 2007 *Colorimetry: Understanding the CIE System* (John Wiley & Sons)
- [48] Lee K-S and El-Sayed M A 2006 Gold and Silver Nanoparticles in Sensing and Imaging: Sensitivity of Plasmon Response to Size, Shape, and Metal Composition *J. Phys. Chem. B* **110** 19220–5
- [49] Fitzner K, Guo Q, Wang J and Kleppa O J 1999 Enthalpies of liquid–liquid mixing in the systems Cu–Ag, Cu–Au and Ag–Au by using an in-situ mixing device in a high temperature single-unit differential calorimeter *J. Alloys Compd.* **291** 190–200
- [50] S. Kealley C, B. Cortie M, I. Maarooft A and Xu X 2009 The versatile colour gamut of coatings of plasmonic metal nanoparticles *Phys. Chem. Chem. Phys.* **11** 5897–902
- [51] James T D, Mulvaney P and Roberts A 2016 The Plasmonic Pixel: Large Area, Wide Gamut Color Reproduction Using Aluminum Nanostructures *Nano Lett.* **16** 3817–23
- [52] Kristensen A, Yang J K W, Bozhevolnyi S I, Link S, Nordlander P, Halas N J and Mortensen N A 2016 Plasmonic colour generation *Nat. Rev. Mater.* **2** 16088