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Tuning the plasmonic response of bimetallic films by laser irradiation

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ABSTRACT

This work shows that surface treatment of multilayer Au and Ag thin films with single UV nanosecond laser pulses is a versatile and an easy-to-use tool for tuning their optical response or colour in a wide spectral range. As a laser parameter, we have varied the fluence. As film parameters, we have studied the film configuration by changing the deposition order, number of layers as well as the composition by varying the thickness of the Au layer while keeping that of Ag constant. The laser exposure produces melting of the layers followed by mixing of the two metals and dewetting, which lead to nanoparticle (NP) formation. The optical response is dominated by the surface plasmon resonance (SPR) associated to the NPs whose wavelength, intensity and bandwidth are consistent with the observed NP morphologies, the number density and the variation of optical constants with Au content. It is dominated by the balance between the interband transition onset of the alloy and the SPR of the nanoalloyed NPs for low fluences and by multipolar interactions for high fluences. While the Au content allows tuning the SPR in the range of ≈180 nm, the laser fluence allows a fine tuning of the SPR features and the film configuration has little impact on the optical response. All together this allows tuning the colour in ranges broader than 20 CIELAB units along the two chromatic axes.

1. Introduction

The use of noble metal nanoparticles (NPs) embedded in a host to make valuable and coloured decorative objects is known since the Roman periods. Nowadays, it is well known that the colours relate to the surface plasmon resonance (SPR) resulting from collective oscillations of surface electrons excited by light [1]. In addition to tailoring colours [2], the consumer goods industry currently focuses to the functionalization or customization of the product thus making surface treatment an important industrial process. Besides, micro and nanostructured metals (including NPs) are receiving special attention due to their potential for applications in many other areas such as photonics, solar cells, catalysis, chemical and/or bio sensors [3,4,5].

In general, the final success of any of these applications depends very much on the capability for tailoring the optical response of the nanostructured material or surface to the application envisaged. There are many ways to do it since it is well known that the SPR features depend on the size, shape and composition of the NPs as well as the surrounding medium and organization [1,3]. Although Ag is the metal exhibiting the best plasmonic response, its poor chemical and structural stability prevents its widespread use especially in non-ideal environments. This problem can be overcome by producing Ag rich mixed Ag–Au nanostructures that have recently shown to have an improved stability and still excellent plasmonic properties [6]. These bi-metallic NPs offer not only the composition but also the structure (nano-alloys or core–shell structures) as extra parameters for tuning the optical response [1,4,5,7,8].

One of the most extended processes to produce metal nanostructured surfaces or NPs on surfaces is the use of thin film technologies for depositing metals on non-wetting substrates (such as glass). Due to the higher surface energy of the metal, it becomes metastable and tends to dewet in order to reduce the energy barrier for low coverages thus leading to island growth. For high coverages, dewetting can be stimulated by thermal annealing to form big NPs. Dewetting is a spontaneous phenomenon that is being proposed to achieve functional materials for several applications [9,10]. The process is well understood and depends on several parameters such as annealing temperature and time, layer thickness or atmosphere [6,10,11]. Laser irradiation with single nanosecond pulses is a fast and easy-to-use alternative method for inducing dewetting and is known to convert metal films into NPs and even self-organized structures with well-defined length scales [7,12,13,14,15,16]. Furthermore, laser irradiation can act remotely and locally in almost any environment as opposed to other surface treatment techniques such as electron or ion irradiation. The laser can in addition easily be focused to different scales. All together this makes laser irradiation an ideal tool for surface treatment and for locally changing colours while preserving the original colour as a background. Actually, locally produced NPs by laser irradiation of Ag-Au multilayer was proposed long time ago as a mechanism for non-erasable optical storage [17].

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The aim of this work is to show that laser irradiation with single nanosecond laser pulses of multilayer metal films is an efficient and versatile tool for producing nano-alloyed NPs that allow tuning the optical response or colour in a wide spectral range. We have used single nanosecond UV pulses to irradiate multilayer films of Au and Ag. The laser fluence, the Ag to Au atomic ratio that is varied through the Au layer initial thickness and the film configuration (deposition order or number of layers) are the parameters studied in order to tune the SPR.

2. Experimental

The samples were prepared by pulsed laser deposition in a turbo pumped vacuum system ($<5 \times 10^{-6}$ mbar) by means of an ArF laser (193 nm wavelength and 20 ns full width half-maximum pulse duration). The laser beam was focused on the targets at an incidence angle of 45° leading to an energy of ≈38 mJ or fluence of ≈2.7 J cm^{-2} per pulse. The repetition rate was fixed at 5 Hz. The substrates were glass slides held at room temperature, positioned at ~38 mm away from the target, rotated along an axis parallel to the plasma expansion axis and shifted a few mm in order to produce a homogenous deposit over an area of ≥1 cm^2. Whereas the number of pulses on the Ag target was kept constant and equal to 2750, that on the Au target was changed in order to vary the overall Au content that we will refer to as [Au]. Generally, Ag was deposited first and Au was deposited on top without breaking the vacuum. This series of samples will be referred to as Au-on-top and includes a reference sample for [Au] = 0, i.e. a sample having a single layer of Ag produced with the same number of pulses. However, for a particular [Au], two additional configurations were studied: an identical bilayer structure but having Au deposited first (Ag-on-top) and a sample having the Ag layer at the centre and one Au layer at either side each produced with half of the number of pulses (tri-layer sample).

In an earlier work [14], we have produced single Ag and Au layers using the same procedure and parameters than in the present work and 2750 and 2500 number of pulses on the Ag and Au targets. Using Rutherford Backscattering, it has been determined that the number of Ag and Au deposited atoms were $n_{at}(Ag) = 3.9 \times 10^{16}$ at cm^{-2} and $n_{at}(Au) = 2.6 \times 10^{16}$ at cm^{-2} that were found to correspond to an effective thickness of 6.6 ± 1.0 nm and 4.7 ± 0.7 nm respectively. Since the number of deposited atoms is proportional to the number of pulses [18] and assuming the rate of sputtering of Ag during deposition of Au (or of Au during deposition of Ag) is similar to the self-sputtering rate, we have used the earlier reported at cm^{-2} to calculate [Au] as $n_{at}(Au)/(n_{at}(Ag) + n_{at}(Au))$. Table 1 summarizes the samples studied in this work and the calculated composition.

The samples were exposed in air to single nanosecond pulses from the same excimer laser using a fly's eye lens homogenizing system manufactured by Laser-Laboratorium Göttingen. The beam intensity was constant (within 5%, mainly related to laser intensity fluctuations) over ≈4 × 4 mm^2 square regions and we have used four irradiation fluences ***F*** up to 295 mJ cm^{-2} that was the highest achievable value. The laser irradiated and non-irradiated regions of the samples will be referred to from now on as laser processed and as-grown regions respectively. The extinction spectra were determined as ln (1/T) from transmittance spectra (T) measured at 0° of incidence angle in the range of 300–800 nm with a UV–Vis Cary 5000 dual beam spectrometer. Finally, as-grown regions and a selection of laser exposed regions were analysed by scanning electron microscopy (SEM) using a JEOL JSM-7500F microscope and observed in gentle beam mode at 1 kV.

Table 1
Sample name, number of laser pulses on the Au target used to produce the sample and Au content of the sample.

Sample name	# on Au	[Au] (%)
Au-on-top-0 (reference)	0	0
Au-on-top-25	1250	25
Au-on-top-32	1750	32
Au-on-top-40	2500	40
Ag-on-top-40	2500	40
Trilayer(Au/Ag/Au)-40	1250 + 1250	40
Au-on-top-52	4000	52
Au-on-top-60	5500	60

3. Results

Fig. 1 shows photographs of Au-on-top series of samples showing both as-grown and laser exposed regions at increasing ***F***. The photographs were taken from the side having the metal on the surface and images taken from the substrate side are almost identical thus evidencing the laser has transformed the whole metal layer. It becomes also evident that the laser exposed regions exhibit a much wider range of colours than the as-grown ones, the colour depending on composition and fluence. This colouring is a consequence of the generally observed break-up of the as-grown regions into NPs as shown in the SEM images included in Fig. 2. Fig. 2 also shows SEM images of as-grown regions evidencing that the initial film structure changes from a discontinuous film close to percolation to an almost continuous layer for the highest [Au] (insets in Fig. 2a and d). This is consistent with the procedure to increase [Au] in this work, i.e. by increasing the Au layer thickness. As fluence increases and for the lowest [Au], big NPs are produced for low fluences (Fig. 2a) that become substituted by smaller NPs for higher fluences (Fig. 2b and c). For the highest [Au], almost no NPs are seen for the lowest fluence (Fig. 2d) while the bilayer has converted into very close and small NPs for all other fluences (Fig. 2e and f). Finally, Fig. 2g–i show the dependence of structure on configuration for the lowest fluence. It is observed that the laser produces big and round NPs in all cases, the only significant difference being the smaller number density of big NPs for the Ag-on-top laser exposed region (Fig. 2h). The comparison of the as-grown regions (insets in Fig. 2g–i) shows that the latter sample is more continuous than the Au-on-top or trilayer ones.

Fig. 3 shows the dependence of the extinction spectra on the several parameters studied in this work. Fig. 3a and b respectively show the spectra of as-grown and laser processed (at 186 mJ cm^{-2}) regions of Au-on top series of samples. The spectra of as-grown regions (Fig. 3a) are featureless with the exception of the cases of the lowest [Au] and reference samples that exhibit a broad band related to the SPR. Both types of spectra are respectively consistent with the almost continuous and discontinuous character of the films. Upon laser exposure (Fig. 3b), a band appears in all samples that is consistent with the SPR of the NPs produced by the laser (see SEM images in Fig. 2) and whose peak shifts

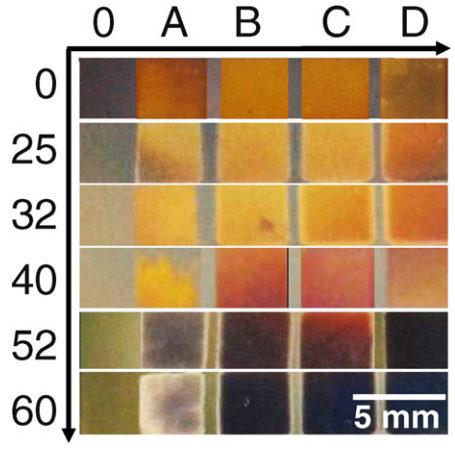

Fig. 1. Optical photographs of the as-grown and laser exposed regions of Au-on-top samples as a function of fluence ***F*** (horizontal axis) and [Au] in % (vertical axis). ***F*** values are as follows: 0 (for as-grown regions), A = 127 mJ cm^{-2}, B = 186 mJ cm^{-2}, C = 263 mJ cm^{-2} and D = 295 mJ cm^{-2}.