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Extended and localized surface plasmons in annealed Au films on glass substrates

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We present here a study on the surface plasmon resonance (SPR) in Au films deposited onto glass substrates and annealed in air at different temperatures. The initial Au films exhibit the resonant absorption of extended surface plasmons which depends on the film thickness. Thermal treatments promote the modification of the continuous films toward the formation of Au isolated islands. The morphological features of the islands depend on the film initial thickness and annealing temperature. The optical properties of the films are qualitatively modified as a consequence of the morphological changes. For films with initial thickness below 30 nm, the islands exhibit localized SPR while thicker films lead to islands large enough to hold extended SPR. © 2010 American Institute of Physics. [doi:10.1063/1.3485825]

I. INTRODUCTION

Surface plasmon resonance (SPR) is probably the most outstanding property of noble metal nanostructures in the form of nanoparticles or thin films. It consists in a collective oscillation of conduction electrons leading to a huge absorption cross section with applications in many fields.^{1–6} In the case of nanoparticles, confined conduction electrons oscillate in resonance with the electromagnetic field leading to localized surface plasmons.^{1,7} For thin films, surface plasmons consist in extended charge waves traveling at the metal-dielectric interface that are excited when their dispersion relation matches that of incident light.^{2–4} While both kind of surface plasmons have been thoroughly studied, scarce research has been carried out at the cross-over region where localized and extended of surface plasmons may coexist.^{8,9} The incorporation of plasmonic nanostructures over surfaces can be used to enhance functionalities and improve their properties. Thin films are commonly used in molecular detection⁵ while gold nanoparticles can increase the efficiency of photovoltaic panels,^{10,11} photocatalytic surfaces,^{12,13} or biological entities labeling devices.^{14,15} However, incorporation of metallic nanostructures over large area surfaces is not straightforward. Dispersion of chemically synthesized nanoparticles is complex and expensive and lithography can hardly achieve areas of hundreds of microns.

Metallic thin films deposited over substrates with poor adhesion are known to exhibit substantial modifications when annealed in air or vacuum including the formation of hillocks, subsequent holes growing, and islands agglomeration leading to a discrete structure.^{16–20} The difference in thermal expansion coefficient between the metal and the substrate leads to the formation of hillocks due to the relaxation of the thermal stress during the course of the annealing process. Higher temperature annealing favors the nucleation and growth of holes by surface diffusion. For temperatures large enough, the holes percolate leading to the formation of Au

islands, which can coalesce during the annealing increasing the average island size in order to reduce the surface energy. While these kind of modifications represent a serious problem for thin film processing in microelectronics,²¹ they can provide a method to engineer their optical properties as surface plasmons are extremely sensitive to the geometry of the nanostructure.^{1,22} Both extended and localized surface plasmons exhibit important changes in the resonant conditions when the size and shape of the nanostructure are modified, thus providing a method to tune the optical properties of the system. This method have been scarcely explored^{11,20} and limited to thin films for the formation of small nanoparticles with localized SPR.

In this work, we study the modification of both extended and localized surface plasmons resonance of Au thin films annealed in air at different temperatures. The transition from a continuous to a discrete structure is reflected in the surface plasmons which switch from extended to localized character. The features of the surface plasmons are determined by the initial film thickness and the annealing process.

II. EXPERIMENTAL

Au films were deposited onto sodalime glass substrates by thermal evaporation. Substrates were cleaned prior to deposition by subsequent immersion in trichloroethylene, acetone, ethanol, and distilled water, and finally dried with N₂ flux. Au films were deposited using a commercial Pfeiffer 306 auto coater. Au wire (99.99% purity, 0.5 mm diameter) was placed onto a tungsten filament with a “V” shape. The wire was initially melted to form a ball at the filament. Substrates were placed at 10 cm from the filament. Deposition was performed under a 10^{−6} torr pressure with currents of 34 A at a rate of 0.167 nm s^{−1}. Samples with thicknesses ranging between 18 and 90 nm were obtained by varying the evaporation time.

The thickness of the samples was routinely determined through their optical transmission, integrated in the range between 400 and 700 nm. We initially used a first set of

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FIG. 1. (Color online) AFM images of 25 nm thickness Au films deposited onto sodalime substrates and annealed at different temperatures in air. Bottom panels present height profiles measured along the lines indicated in the panels.

samples, whose thicknesses were directly measured using low angle x ray reflectivity. The calibration curve obtained in this way, relating total optical transmission and film thickness in the first set of samples, was used to further determine the thickness of the rest of the films.

Thermal treatments were performed in air and consisted in (a) an initial stage of 2 h, where temperature was gradually increased from 300 K to the target temperature, (b) 3 h at constant temperature, and (c) a last cooling stage where temperature gradually decreased, during a time interval of about 8 h until the sample reached room temperature.

Optical absorption spectra in transmission mode were recorded with a Shimadzu UV-1603 double beam spectrophotometer. Extended SPR was measured in the attenuated total reflectance (ATR) mode in the Kretschmann–Raether configuration⁴ using a home-made device. The light source was a 1.5 mW He–Ne polarized laser ($\lambda=632.8$ nm) in a p-polarization geometry with respect to the gold surface. The glass substrate with the gold film was attached to a triangular borosilicate prism by using an index matching gel and mounted onto a rotating platform. The reflection spectra are represented as a function of the external incident angle (and not in terms of the internal angle inside the prism). The reflected light was collected with a large elongated Hamamatsu photodiode to avoid moving the detector during the measurements. The laser beam was modulated with an optical chopper, and the signal collected with the photodiode was measured with a lock-in amplifier using as reference signal that of the optical chopper. Data were collected with a computer using a home-made VISUAL BASIC code.

Atomic force microscopy (AFM) images were taken with a Nanotec instrument in air, using a silicon tip, in non-contact mode and at room temperature. The images were analyzed with the WSXM software package from Nanotec.²³ Optical microscopy images were obtained using a Zeiss Axiohot microscope.

Simulations of the intensity of the reflected beam were

performed with a home-made code solving the Fresnel equations for the system. The code includes the correction, to account for both reflection and refraction of the coupling prism. The proper performance of the code was tested with available programs.²⁴

III. RESULTS AND DISCUSSION

A. Morphology of the films

It is well known that the morphological features of the film depend mainly on the initial film thickness and annealing atmosphere, time, and temperature.¹⁶ However, previous studies have shown that an almost stationary situation is achieved for annealing times over 120 min.^{16–18} Moreover, the use of atmospheres rich in oxygen accelerates the morphological modifications as it favors the surface diffusion mechanism.¹⁸ Thus, the time of our annealing processes is assumed to be large enough to reach the almost stationary situation and we focus our study on the effect of initial thickness and annealing temperature.

Figure 1 shows the AFM images for the 25 nm sample. The as-grown sample exhibits a continuous surface with rms roughness of 4.6 nm and grain size at about 30 nm. After annealing at 300 °C, the film exhibits the presence of hillocks with an almost continuous structure formed by grains that can be resolved in the image. Grain size distribution results very broad, with grains in the range from 100 to 400 nm. At some points the glass substrate is observed, although the area of uncovered substrate scarcely reaches 10% of the total specimen.

Annealing at 400 °C induces the grain growth with an average size at about 300–400 nm and 80–120 nm height, and the uncovered area represents 20% of the surface. Increasing the annealing temperature up to 500 °C leads to even larger grains with a typical lateral size of 500 nm and a height of 100 nm. A larger fraction of uncovered surface (at about 30%) is seen as well. For this annealing temperature,

FIG. 2. (Color online) AFM images of 45 nm thickness Au films deposited onto sodalime substrates and annealed at different temperatures in air. Bottom panels present height profiles measured along the lines indicated in the panels.

the uncovered areas percolate and the Au islands become mainly isolated. The Au volume in the annealed samples differs less than 10% and does not show a clear tendency, suggesting that these differences may be attributed to experimental uncertainties. Thus, we may conclude there is no significant Au removal during the annealing process within this resolution.

The images corresponding to the film with 45 nm thickness are presented in Fig. 2. The as-deposited film exhibits morphology very similar to that of 25 nm thickness, with rms roughness of the order of 1.4 nm. Annealing at 300 °C leads to the formation of hillocks with hill-to-valley height differences of the order of 20 nm. Due to the larger film thickness, at this temperature there is no grain separation or holes nucleation as evidenced by the AFM images. Annealing at 400 °C promotes the formation and percolation of holes and Au islands leading to a discrete structure of the film. The uncovered area is roughly the 50% of the sample surface and the average size of the Au island is of the order of the micron. Most islands exhibit elongated shape with an average height of 150 nm. Annealing at 500 °C increases the uncovered area up to 70% of the sample and the Au islands become more rounded. Their height increases to an average value of 200 nm.

Films with initial thicknesses of 18, 70, and 90 nm were also studied, exhibiting a similar phenomenology to that of the 25 and 45 nm ones, although quantitative results are different.

The films with the largest Au islands can be observed by optical microscopy. As an example, Fig. 3 shows the optical image for the 90 nm thickness sample annealed at 500 °C.

AFM images are not shown for all the studied samples, but the main results derived from their analysis are presented in Fig. 4. In order to study the effect of film thickness and annealing temperature on the film morphology we determined four parameters from the AFM images: island size and height, catchment area, and uncovered surface. Catchment

area¹⁸ is defined as the area from where the metal atoms migrate to form a single island and is approximately d^2 , being d the mean interisland distance.

As Fig. 4 evidences, the morphological features of the samples depend on both annealing temperature and initial film thickness, being the later the more relevant parameter. Modification of morphology in metallic thin films upon annealing has been studied for long time.^{16–21,25,26} Briefly, the difference in thermal expansion coefficient between the substrate and the metal is the main responsible of the process. The inhomogeneous stress distribution at the film-substrate interface promotes the migration of the film over the stressed areas to a more relaxed one. The prolonged hillock growing finally induces the appearance of some holes. Subsequent hole growth which takes place mainly through surface diffusion. Finally holes percolate leading to the formation of metal islands. For annealing temperatures and time large enough, the islands tend to modify their shape becoming more rounded in order to reduce their surface energy. The morphology of the film at the different stages of the process

FIG. 3. Optical microscope image of a Au film, with an initial thickness of 90 nm, deposited onto a sodalime substrate and annealed at 500 °C.

FIG. 4. (Color online) Morphological parameters of the films derived from AFM images as a function of annealing time and initial film thickness.

depends on the initial film thickness and annealing atmosphere, time and temperature.

The formation of the holes becomes easier as thin film decreases, because the material to be displaced to create a hole is smaller. Actually, for the 18 and 25 nm films holes were observed just after 300 °C annealing while thicker films showed only the presence of holes upon annealing at 400 °C. For thinner films a larger number of holes nucleate and percolate leading to the formation of small islands with limited size and height and reducing the catchments area as Fig. 4 evidences. On the contrary, for thicker films, the fraction of uncovered surface depends mainly on the annealing temperature and does not depend so significantly on the film

thickness provided the annealing temperature is high enough (see data after annealing at 500 °C).

B. Optical properties

The optical measurements show the existence of both extended and localized surface plasmons in the samples. Figure 5 presents the curve of extended SPR for the studied samples. Extended SPR, measured by ATR method in the Kretschmann–Raether configuration, can be optimally excited for a thickness range around 50 nm.⁴ Thinner films exhibit reduced resonance due to the destructive interference between the incident and the backscattered beams, while for thicker films the transmission of the incident light decreases exponentially across the film leading to a weak electromagnetic field at the metal/dielectric interface.

Comparing the as-grown samples, we observe the resonant curve is narrower for the 45 nm film than for the rest. For the 25 nm film, the resonance curve is very wide (due to the extra damping introduced by the interference between incident and backscattered beam) while thicker films exhibit a narrower but weaker SPR curve. Actually, this dependence of the resonance curve upon film thickness is in agreement with the spectra calculated for the films with the thickness of the as-grown samples (Fig. 6).

The differences in intensity between the calculated and experimental spectra can be explained as due to the surface roughness of the films which is known to damp to SPR bands reducing the intensity and widening the absorption band.⁴

Samples annealed at 300 °C exhibit wider and weaker SPR curve than the corresponding as-grown ones for all the samples except that of 25 nm. For this later, the thermal treatment increases both width and intensity of the absorption band. The presence of the extended SPR band after annealing at 300 °C is in agreement with the AFM studied showing that films exhibited a continuous structure after annealing at this temperature. The formation of hillocks after the thermal treatment increases the surface roughness leading to damped plasmons that account of the increase in bandwidth. The increase in SPR intensity after annealing in this sample could be related to the larger film thickness in certain regions evidenced in AFM images (see Fig. 2).

Upon annealing at 400 and 500 °C the extended SPR band is almost inappreciable in the spectra irrespective of the initial film thickness as expected for films showing a discrete structure with dimensions significantly smaller than light wavelength. It is worthy noting that the SPR measurements in the Kretschmann–Raether configuration can just excite the SPR characteristic of continuous films, but the absence of resonance in these measurements does not imply that no SPR can be excited in the nanostructures. Actually, patterned films exhibit SPR with features that depend on the patterning geometry.^{2,27} However, the spectra for the 70 nm film after annealing at 400 °C still exhibit an extended SPR band although it is very wide and weak. For this sample, island size and height is about 1000 nm and 150 nm, respectively. With this thickness it is still possible to excite SPR in the used configuration. Moreover, the 150 nm height is the average one, but there are islands with smaller height. The island size

FIG. 5. (Color online) Extended SPR curves measured in the ATR mode (Kretschmann–Raether configuration) for the films with different thickness (a) 25 nm, (b) 45 nm, (c) 70 nm, and (d) 90 nm, upon annealing at different temperatures.

of 1000 nm is larger than the light wavelength and the large anisotropy of the islands (similar to that Fig. 2) can lead to islands large enough to hold SPR in certain directions with a dispersion relation similar to that of continuous films. An-

FIG. 6. (Color online) Calculated SPR spectra for Au films with different thickness onto sodalime glass ($n=1.5$).

nealing at 500 °C lead to more rounded islands reducing the larger dimension, therefore, reducing the absorption due to extended SPR as experimentally observed.

Optical absorption spectra of the studied samples are presented in Fig. 7. The absorption edge at about 300 nm is due to the sodalime substrate and cannot be identified with any feature related to Au islands, while the minimum at about 500 nm is characteristic of bulk gold (and responsible of the yellowish coloration of this metal).²⁷ The shoulder in the range 400–500 nm is due to interband transitions (promoting electrons from the 3d band to the Fermi level).²⁸

For the 25 nm film, the absorption band characteristic of Au nanoparticles at about 540 nm is clearly observed after annealing at 400 °C. This result is in agreement with the AFM images showing that annealing at this temperature leads to a discrete film with Au nanoparticles. Annealing at 500 °C yields a blueshift and narrowing of the absorption band. Main morphological difference between the 25 nm thickness samples annealed at 400 and 500 °C is the particle distance (see Fig. 1). The short interparticle distance in the sample annealed at 400 °C favors the dipolar interaction between adjacent particles which is known to wide and redshift the SPR.^{1,22} Annealing at 500 °C increases the distance between particles leading to a SPR band more similar to that expected for isolated Au nanoparticles. Samples with initial film thickness 45 nm and above did not show a clear SPR absorption band irrespective of the annealing temperature (in the studied range). We analyzed also a sample with 30 nm initial thickness that neither shows the absorption band of localized SPR upon annealing at different temperatures. Thus, we conclude 30 nm is the upper thickness limit to obtain Au islands exhibiting localized SPR for sodalime substrates.

For thicker samples (i.e., 45 nm and above) the main effect of annealing is the decrease in the absorption coefficient in the whole spectral range, which is clearly observed for those films annealed at 400 and 500 °C [green and blue curves in Figs. 7(b)–7(d)]. A magnified view of these spectra, on the other hand, does not reveal any qualitative difference with respect to the corresponding spectra before the annealing. The drastic modification of the absorption coefficient is due to the formation of holes, providing paths where the light beam crosses without interacting with the Au nanostructures. Actually, the evolution of the absorption coefficient is in-

FIG. 7. (Color online) Optical absorption spectra for the films with different thickness (a) 25 nm, (b) 45 nm, (c) 70 nm, and (d) 90 nm, after annealing at different temperatures.

verse to that of the uncovered area presented in Fig. 4. Thus, we conclude that the islands exhibit a bulk character from an optical point of view, and they do not exhibit the absorption associated to the localized SPR.

Consequently, for the sample with 25 nm initial thickness we observe a clear transition between localized and extended SPR. The cross-over region is achieved upon anneal-

ing at 300 °C. For this annealing temperature, the spectra exhibit features different to those expected for pure localized and extended SPR. The optical absorption spectra of this sample [Fig. 7(a)] does not exhibit the clear maximum at about 600 nm characteristic of localized SPR (as those observed for the samples annealed at 400 and 500 °C) but a plateau extended up to the NIR region. Cesario *et al.*⁸ recently demonstrated that interaction between localized and extended surface plasmons induce changes in the optical absorption spectra for gold nanoparticles in the proximity of a continuous silver thin film due to SPR interaction. Reducing the distance between the nanoparticles and the film, the absorption spectra flattens as we observed here. As concerns the extended SPR, the unexpected shift toward larger angles (i.e., larger k value) and the increase in the intensity of the resonance observed annealing at 300 °C the sample with initial thickness of 25 nm [Fig. 5(a)] can also be related to the interaction between localized and extended SPR. Murray *et al.*⁹ performed dispersion measurements on silver films with holes, ranging from metal percolation to island percolations. They found important changes in the k resonant values and modification in the intensity of the resonant condition in the cross-over percolation region. Therefore, beside the well defined regions of localized and extended surface plasmons we find a cross-over region where both kinds of excitation may coexist, interacting and providing new phenomenology that needs to be further investigated.

IV. CONCLUSIONS

Au thin films with thickness in the range from 18 to 90 nm were deposited onto glass substrates and annealed in air at different temperatures. The thermal treatment promotes the morphological modification of the films leading to a discrete structure of Au islands. The island sizes, shape, height, and interisland distance depend of the film initial thickness and annealing temperature. Structural modifications lead to dramatical changes in the optical properties of the films. Optical response depends on the relative size of the Au islands and the light wavelength. For films with initial thickness up to 30 nm, the Au islands exhibit the absorption associated to localized SPR. Thicker films lead, upon annealing, to large islands (dimensions larger than visible light wavelength) able to hold extended SPR. Therefore, annealing Au films deposited onto glass provides a method to tune the plasmonic properties of the films in a wide a range and over large areas not easily achievable by other methods.

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