Electric field assisted dissolution of metal clusters in metal island films for photonic heterostructures

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Abstract

The dissolution of metal clusters in metal island films by the simultaneous application of electric field and temperature is reported. The consequent fading of surface plasmon resonance greatly modifies the optical properties of the samples. The dissolution process is verified in island films of different metals, obtained under different conditions and covered by different dielectric materials, as well as on multilayer dielectric stacks showing interferential properties. The tailoring possibilities of the optical behavior of metal island films combined with the inexpensive technical requirements of this approach opens up the possibility to produce low-cost photonic heterostructures.

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Metal island films (MIFs) can be considered as two-dimensional ensembles of metal clusters deposited on a solid substrate and one of the most easy-to-prepare cases of nanostructured matter. They can be obtained simply, during the first stage of evaporation process, when the deposited mass thickness of metal is in the range of few nanometers. These films show a unique optical behavior due to the surface plasmon (SP) resonance of free electrons in clusters. SP properties of MIFs can be easily and widely tailored using different methods, like two-step evaporation of metal compounds[1], coating of MIF with a dielectric layer[2] or modification of the deposition conditions that result in a variation of the geometrical arrangement of clusters at nanoscale[3]. Consequently, MIFs are used in many optical applications like selective absorbers, optical polarizers and data storage[4-6] or in chemical and biological sensing and surface enhanced spectroscopy[7,8]. On the other hand, the potential SP-related applications of metallodielectric media have been extended with the capacity to structure matter at microscopic level leading to the production of devices ranging from plasmonic waveguides[9] to gratings[10]. In this framework, the electric field assisted dissolution (EFAD) of metal nanoparticles has been recently proposed. It has been shown that simultaneous application of static electric field and moderately elevated temperatures induces dissolution of metallic nanoparticles embedded in a glass matrix[11,12] or silica film[13]. Such dissolution process follows from the ionization of metal nanoclusters and the later ejection of metal ions from the nanocluster. Applying an electric field with patterned electrodes, two-dimensional photonic structures have been produced by EFAD[14].

In the present study we report the dissolution of metal nanoclusters in metal island films by application of electric field and temperature. The consequent modification of optical properties, due to the absence of SP resonance, makes possible to expand the range of potential applications of EFAD technique and MIFs. Indeed, this result shows that the presence of a depth-distribution of metallic clusters in the direction of the applied electric field, as in metal nanoparticles-containing glasses or films, is not required to induce the EFAD process. This aspect is particularly relevant for miniaturization purposes and surface structuring. Moreover, MIFs have a highly and easily tunable optical behavior, compared to glasses or silica films containing metal clusters, in which SP tuning is limited by the dielectric nature of the media surrounding the clusters. In addition, since MIFs can be easily embedded in multilayer stacks, EFAD may permit structuring samples combining interferential properties of optical coatings with SP absorption of clusters.

Silver MIFs of 7 nm mass thickness, covered with 7 nm thick SiO_2 or TiO_2 layers, were deposited on 1 mm thick N-BK7 borosilicate glass substrates by reactive electron beam evaporation at substrate temperatures of 25 °C or 220 °C. All samples show a bluish coloration in reflection caused by SP absorption

in MIF. Coloration of samples varies due to different SP characteristics (Figure 1). Samples deposited on colder substrates are red-shifted and have a broader SP absorption owing to the high disorder, percolation and non-sphericity degrees of clusters typically grown at low temperatures[3,15]. Besides, SP of samples coated by TiO_2 are red shifted with respect to those coated by SiO_2 due to the higher dielectric constant of clusters surroundings[2,16]. Each sample was annealed at 300°C in air for two hours. Simultaneously, a constant voltage of 1 kV was applied, with the MIF facing the anode. As anode, it was used a Cr thin film deposited on a glass substrate that was previously masked, leaving part of the glass uncoated. In this way, one part of the treated sample was under the influence of electric field and temperature (zone A) and the other part, only of temperature (zone B). After the treatment, the bluish coloration of the untreated samples disappeared in zone A, that became completely bleached and remained in zone B only (Figure 1). For all the samples, complete absence of SP absorption occurs in zone A, having a transmittance similar to the one of bare N-BK7 substrate. Slight interference fringes are seen in these optical spectra that can be attributed to different concentration of ions through the substrate depth caused by effect of electric field and temperature, as in thermal poling of glass. Consequently, a small refractive index gradient appears in the substrate[17], giving place to weak interferential effects. Spectra of zones B show narrower SP absorption with respect to the untreated samples that can be associated to the increase of clusters sphericity upon thermal annealing[18,19].

The optical modifications in the zone A of the samples can be explained by the dissolution of silver clusters caused by the treatment, resulting in the absence of SP absorption. In order to confirm the cluster dissolution, plain view high angular annular dark field (HAADF or Z-STEM) micrographs of the surface of the sample having a MIF covered by TiO_2 and deposited on colder substrate were taken with a Jeol2010F field-emission Gun Microscope (Figure 2). Z-STEM micrographs allow distinguishing slight differences in atomic number (Z) as the intensity shown is approximately proportional to Z^2. Taking into account that Ag has Z=47 and that Z_{mean} of TiO_2 is 12.7, it can be expected to observe the Ag nanoparticles with a high bright intensity. In this way, in Figure 2.b, it can be seen that in zone B there is a homogenous distribution of bright islands, predominantly not percolated and with an average diameter of 12 ± 3 nm and a density of $5.4 \cdot 10^{11}$ island/cm^2. In zone A (Figure 2.a) no bright clusters can be observed. Electron energy loss spectra (EELS) were taken at both zones, confirming the presence of Ti atoms on the sample surface for both cases while Ag was found only in zone B, confirming that the bright islands were indeed silver metal clusters. Furthermore, the absence of metal in zone A is supported by the induction of sample electronic charging during the measurements.

Thus, the sample surface was easily damaged by the electron beam few seconds upon beginning of the exposure, as shown in Figure 2.a. ,

The dissolution process can be explained in terms of the basic principle of EFAD[11-13]: under the influence of high electric field, silver clusters are ionized, with electrons tunneling to the anode. The positively charged silver ions can be then ejected from the silver cluster into the substrate due to the electric field, leaving uncharged clusters. This process continues until the cluster is completely dissolved. In order to get a more clear insight of the dissolution process, voltages from 200 V to 1 kV were applied to samples in 200 V steps of 20 min at 300 °C. The electrical current passing through the sample was measured for a bare N-BK7 substrate and for substrate having Ag MIF coated with SiO_2 (Figure 3). At each new voltage step, the current increased, followed by a slow current reduction as an ion-depleted region is formed preventing the drift of ions (basically Na^+) and decreasing the sample conductivity[20]. At low voltages, the current through the N-BK7 substrate having a MIF is lower than for the bare substrate, due to the higher resistivity of the MIF coated layer[13]. As the voltage increases, the cluster dissolution process initiates, with decreasing resistivity of MIF and finally the N-BK7 sample with MIF presents similar current values to the bare N-BK7. Additionally, the observed current decrease due to the formation of an ion-depleted region is smaller for the sample with MIF than for the bare N-BK7 substrate. This difference can be explained by the supply of silver ions into the region depleted of Na^+, for the sample with MIF. On the contrary to previous studies[21], no formation of a percolated silver layer was observed, possibly due to the low amount of metal in a MIF compared to the typical Ag distribution in metal-doped glasses. However, the presence of ions in the substrate depth has been confirmed by appearance of weak surface plasmon absorption after annealing of the treated samples at high temperatures (500 °C), due to re-aggregation of silver ions into clusters, as reported in reference [11].

In addition to the experiments with silver, gold and copper MIFs of 7 nm mass thickness were deposited on N-BK7 substrates, covered with SiO_2 or TiO_2 and treated as described above. Bleaching was also achieved, with samples with Cu MIFs requiring shorter treatment times for the complete bleaching in comparison with Ag MIFs, while for Au MIFs samples the bleaching was incomplete. Application of higher electric field to the Au MIFs samples results in lower SP absorption. Also, no bleaching of samples having Ag MIF was observed if applied voltages were below 500 V or temperatures lower than 250 °C. The diversity of results of the bleaching efficiency depending on clusters material and treatment conditions can be associated to the differences in ionization energies of different metals[22], but also to the shape, size and concentration of

metal in the MIF, and on the dielectric environment. The precise dependence of the temperature and voltage thresholds for the dissolution process with the sample properties is subject of current research.

In order to examine the possibility of combining interferential properties of coatings with SP absorption, a multilayer stack with alternating layers of MIF and dielectric films was deposited. The sample heterostructure was N-BK7/$(SiO_2/Ag/TiO_2/Ag)^4/SiO_2/Ag/TiO_2$, where SiO_2 and TiO_2 layers were 15 and 29 nm thick respectively and Ag MIFs mass thickness was 7 nm. The transmission of this untreated sample (Figure 4) is below 10% in the whole visible range due to SP absorption of MIFs. Bleaching of the sample was achieved by application of EFAD technique in the zone A while in zone B remained high absorption. Interferential behavior can be seen in the spectrum of the bleached zone due to the alternating structure of SiO_2 and TiO_2 films. For comparison, computed transmittance of an equivalent heterostructure of SiO_2 and TiO_2 films, representing the deposited multilayer stack without the MIFs, is shown. The spectral position of transmittance maxima and minima of the simulation agrees with experimental data. However, experimental transmission is lower probably due to rough interfaces between SiO_2 and TiO_2 layers as result of dissolution of the embedded MIFs that increase scattering losses. Nonetheless, this result confirms the possibility to combine the dissolution of metallic clusters and SP absorption with the interferential properties of multilayer stacks.

In summary, the EFAD of nanoclusters in metal island films is demonstrated. The dissolution process has been achieved in samples with different SP properties, due to differences in islands material (Ag, Au, Cu), dielectric material coating (SiO_2, TiO_2) or the geometry of clusters depending on the deposition temperature. As first, the study shows that EFAD can take place in these two-dimensional systems, without presence of a clusters depth-distribution in the direction of the applied electric field, what might be valuable for device miniaturization and surface nanostructuring. Furthermore, the possibility to apply this technique to MIFs embedded in multilayer stack is also shown, enabling the combination of SP absorption with interferential properties of multilayers in the same sample. Overall, the inexpensive requirements of the EFAD technique, in addition to the simple manufacture and high degree of tuning of optical behavior of MIF, opens up the possibility to obtain low-cost and mass-production photonic and plasmonic structures.

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Figure Captions

Figure 1: Optical extinction spectra of Ag MIF samples coated by SiO_2 (a, b) and TiO_2 (c, d) deposited at 25°C (a, c) and 220 °C (b, d) before the treatment (solid line) and of the zones A (dashed) and B (dotted) after the treatment. Inset shows photo of sample zones A and B after the treatment.

Figure 2: Z-STEM micrographs of the zones A (a) and B (b) of a treated sample having an Ag MIF coated by TiO_2 and deposited at 25°C. The black lines on a) correspond to beam damage from EELS measurements due to sample electronic charging.

Figure 3: Current evolution at applied voltages of 200, 400, 600, 800 and 1000 V for a N-BK7 substrate (dashed line) and a N-BK7 substrate with Ag MIF coated with SiO_2 (solid line).

Figure 4: Transmittance spectra of a multilayer structure of SiO_2 and TiO_2 layers with Ag MIF films between each interface as deposited (solid) and for zones A (dashed) and B (dotted) after 2 hours of treatment. Dash-dotted line shows the simulation of the optical transmittance of the equivalent SiO_2/TiO_2 structure without MIFs.

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Figure 1

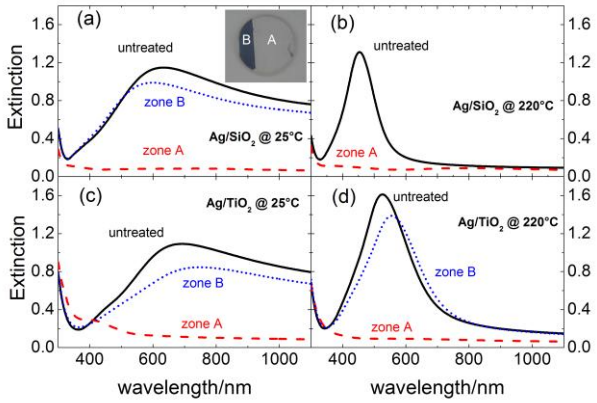

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Figure 2

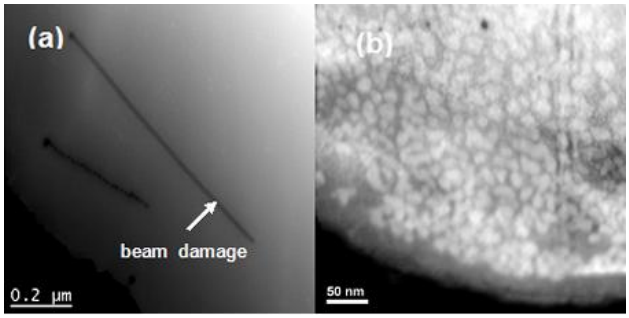

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Figure 3

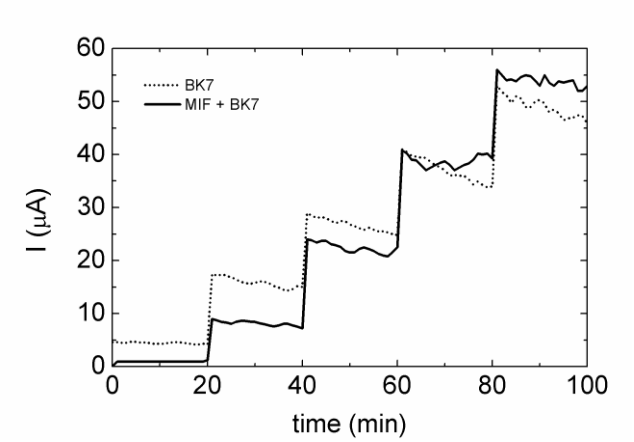

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Figure 4