Modification of optical properties of metal island films by electric field assisted dissolution of clusters

J. Sancho-Parramon *[a], V. Janicki[a], H. Zorc[a], M. Lončarić[a]
[a]Ruđer Bošković Institute, Bijenička c. 54, Zagreb 10000, Croatia

ABSTRACT

Metal island films show unique optical properties owing to the local surface plasmon resonance of islands free electrons. In the present study, the electric field assisted dissolution of clusters in metal island films is reported. Island films of Au, Ag, and Cu are deposited under different conditions by thermal evaporation and coated with thin dielectric layers. The samples are treated with the simultaneous application of an intense electric field and temperature, leading to the sample partial or total bleaching due to the dissolution of metal clusters in the films. Owing the facility of production of metal island films and the inexpensive technical requirements of the dissolution process, this approach suggests a novel path for the production of low-cost photonic structures.

Keywords: metal island films, surface plasmon, electric field assisted dissolution

1. INTRODUCTION

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 local surface plasmon (SP) resonance of free electrons in clusters. SP properties can be easily 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[3]. Consequently, MIFs are used in many optical applications like selective absorbers, optical polarizers or data storage[4]. In addition, the strong local field enhancement that takes place in the vicinity of optically excited clusters can be used in chemical and biological sensing and surface enhanced spectroscopy[5]. On the other hand, the potential SP-related applications of metallodielectric media have been extended with the capacity to structure matter at microscopic level. In particular, nanostructuring points towards the production of subwavelength structures like plasmonic waveguides[6]. Microstructuring enables fabrication of advanced optical elements like gratings or segmented filters[7]. In this framework, the electric field assisted dissolution of metal nanoparticles (EFAD) has been recently proposed as a promising structuring technique. 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[8,9] or silica film[10]. Such dissolution process follows from the ionization of metal clusters and the latter ejection of metal ions from the cluster. Applying an electric field with patterned electrodes, two-dimensional photonic structures have been produced by EFAD[11,12]. Owing to its simplicity and inexpensive technical requirements, this method represents an appealing possibility for production of low-cost plasmon-based photonic structures.

We have recently demonstrated the possibility to perform EFAD of metal clusters in MIFs[13]. This result makes possible to expand the range of potential structuring applications of EFAD technique. Indeed, MIFs have a highly and easily tunable optical behavior, particularly when 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 the present study we report the dissolution of clusters in different types of metal island films obtained by thermal evaporation. In the next section we describe experimental details for deposition and EFAD treatment. In Section 3, we present the results for the optical properties of the as-deposited samples and discuss the differences in optical behavior in terms of the MIFs material and manufacturing conditions. Section 4 shows results of the EFAD treatment and the cluster dissolution efficiency for different MIFs is discussed. Finally, the key results of the study are summarized in the concluding Section.

*j.sancho.parramon@gmail.com; fax +385-1-4680-104

2. EXPERIMENTAL

2.1 Metal island films obtained by thermal evaporation

Metal island films of different metals (Ag, Au, Cu) were deposited on 1-mm thick BK7 borosilicate glass substrates by e-beam evaporation in a Varian 3117 deposition chamber. The MIFs were coated by a dielectric layer (SiO_2 or TiO_2) in order to modify the SP properties and to prevent oxidation of metal clusters. Mass thickness of both MIF and dielectric coating layer was 7 nm and was controlled by quartz crystal monitoring. In order to further modify the optical properties, samples were obtained at two different substrates temperatures: 25°C and 220°C.

2.2 Electric field assisted dissolution treatment

The samples were annealed at 300°C in air atmosphere for two hours. Simultaneously, a constant voltage of 1 kV was applied to the sample, with the MIF facing the anode. Chromium single layers (720 nm thick) were deposited on glass substrates to be used as electrodes. Previous to the deposition, a mask was placed on the substrate to leave part of the glass uncoated. In this way, part of the sample was under the influence of electric field and temperature (zone A) and the other part, only of temperature (zone B). Electric field was applied to the samples using a high voltage power supply (246 High Voltage Supply, Keithley Instruments) and the treatment was performed in a home-made oven controlled by a NiCr-NiAl thermocouple. A sketch of the experimental setup for the electric field assisted dissolution treatment is shown in Fig. 1.

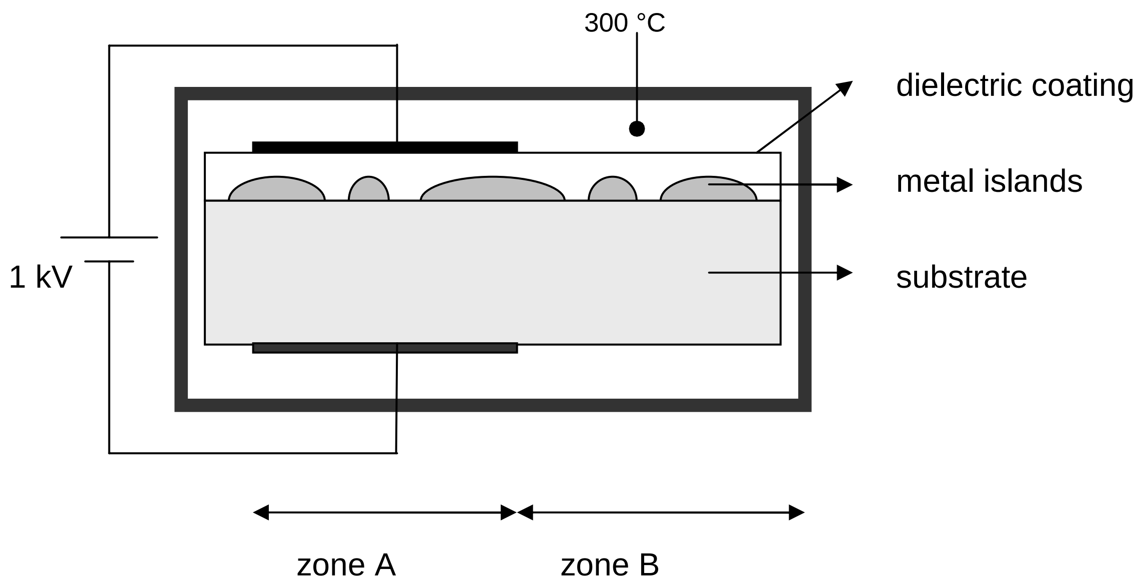


Fig.1. Sketch of the experimental configuration for electric field assisted dissolution treatment.

Optical transmittance spectra of both as-deposited and EFAD-treated samples were taken with a Perkin Elmer Lambda 25 spectrophotometer in the UV-VIS-NIR range (300-1100 nm) with a wavelength resolution of 1 nm.

3. OPTICAL PROPERTIES OF AS-DEPOSITED SAMPLES

The optical properties in the spectral range of interest are dominated for all the samples by the SP resonance of clusters free electrons. The SP absorption is evidenced by a deep in transmission spectra, as shown in Figures 2 and 3 for Ag and Au/Cu metal island films respectively.

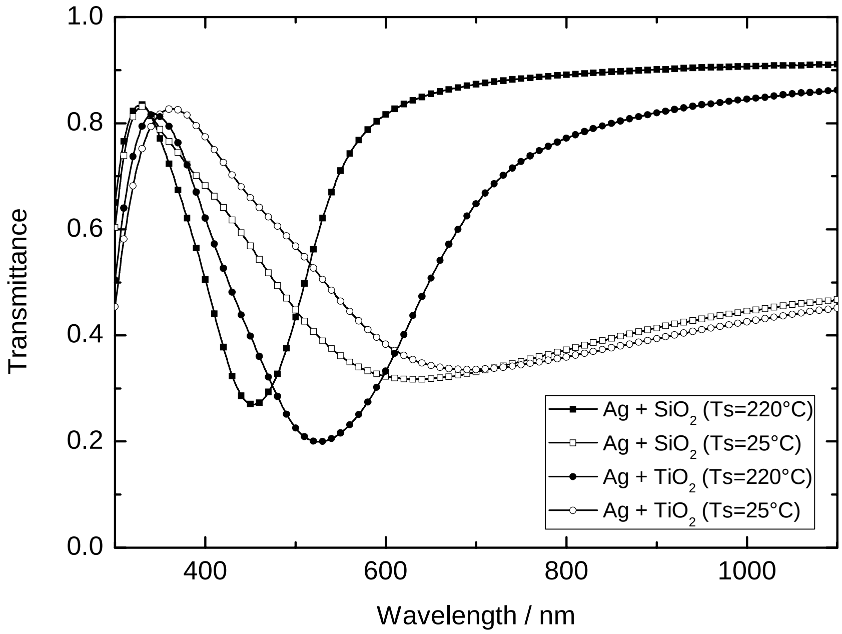


Fig. 2. Transmittance spectra of samples with Ag metal island films obtained under different conditions: at hot substrate (220 °C) and coated with SiO_2 (solid squares) or TiO_2 (solid circles) and at cold substrate and coated with SiO_2 (open squares) or TiO_2 (open circles).

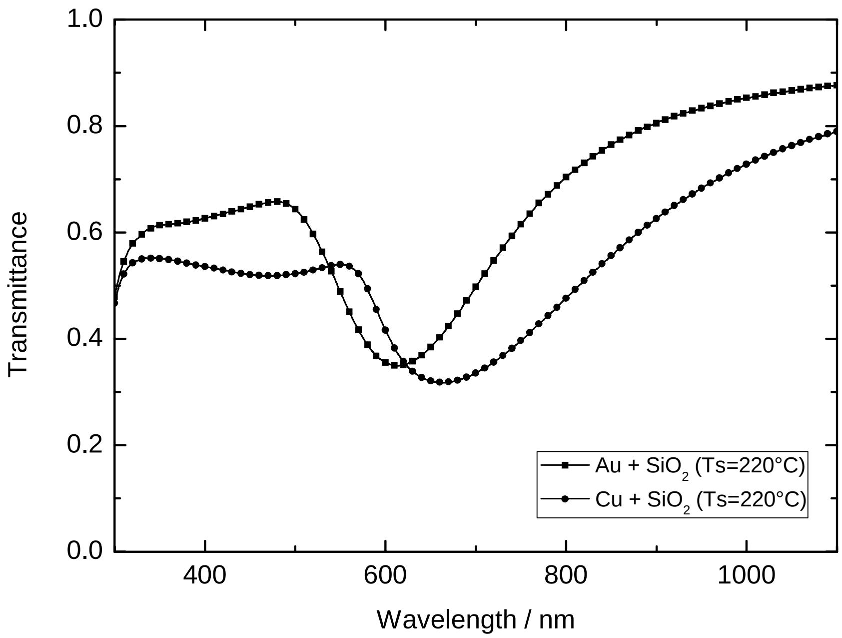


Fig. 3. Transmittance spectra of samples with Au (squares) and Cu (circles) metal island films obtained at hot substrates (220°C) and coated with SiO_2.

In order to understand the diverse optical behavior of different samples from a qualitative point of view, we shall first consider that the surface plasmon resonance condition for a single small spherical metal particle with dielectric constant ε_M embedded in a dielectric host with dielectric constant ε_H is given by[14,15]:

$$\left|\varepsilon_M + 2\varepsilon_H\right| \to 0 \qquad (1)$$

The dispersion of the optical constants (real and imaginary parts of the dielectric function) of the used metals is represented in Fig. 4.a., while in Fig. 4.b., the quantity $\left|\varepsilon_M+2\varepsilon_H\right|$ has been represented considering SiO_2 as the dielectric host (ε_M=2.3).

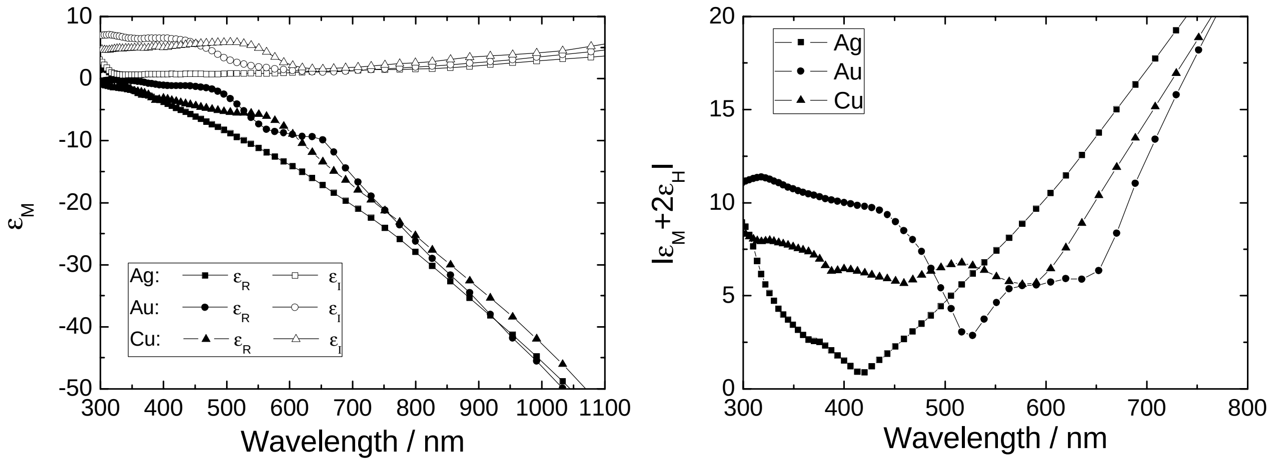


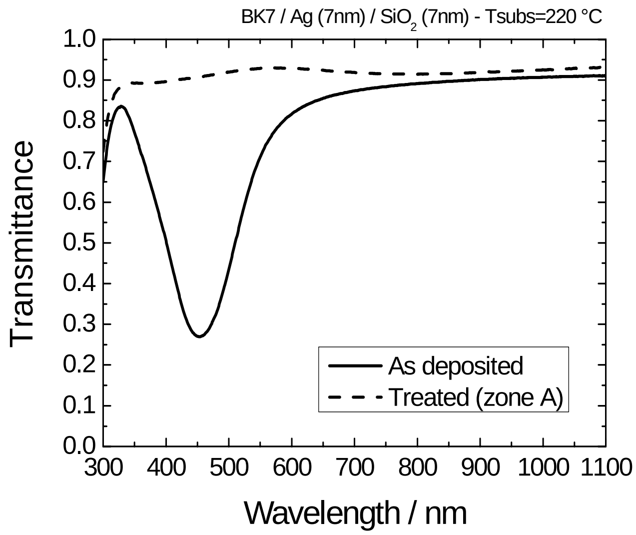
Fig. 4. a) (left) Optical constants of the used metals taken from reference 16 b) (right) Resonance condition for the used metals and assuming a SiO_2 environment for the metal clusters (ε_M=2.3)

The data represented in Fig 4.b can be used to understand qualitatively the differences observed for the SP characteristics of metals island films. First, the wavelength of the minimum of $\left|\varepsilon_M+2\varepsilon_H\right|$ is close to the wavelength value where the minimum in transmission spectra of metal island films occurs. For Ag, the resonance condition is best accomplished because the imaginary part of the dielectric function of Ag is close to zero in the whole visible. This is not the case for Au and Cu, where there is a contribution to the imaginary part of the dielectric function at short wavelengths due to electronic interband transitions. As result, the minimum of $\left|\varepsilon_M+2\varepsilon_H\right|$ is broader than and not as deep as for Ag. Consequently, the SP absorption is broader and less deep for Cu and Au than for Ag.

From the dielectric function of Ag, it can be understood also the blue shift of SP for Ag metal islands coated by SiO_2 with respect to those coated by TiO_2. As TiO_2 has a higher dielectric constant than SiO_2, the resonance condition will occur for more negative values of the real part of the dielectric constant of Ag, i.e., at longer wavelengths. The analysis of the resonance condition for single small spherical particles, however, can not explain the changes on the SP characteristics depending on the substrate temperature. These changes must be attributed to the modification of the geometrical arrangement of the metal clusters depending on the substrate temperature. Indeed, clusters grown at cold substrates typically present a wider size and shape distribution and higher percolation degree[17], resulting in an increase of the cluster-cluster interaction and leading to a broader SP resonance[18,19].

4. OPTICAL PROPERTIES OF EFAD-TREATED SAMPLES

The optical properties of the samples after treatment are shown in Figures 5 to 10. The most remarkable observation is that the SP absorption disappear or significantly decreased in the zone A of the samples (i.e., under the influence of electric field and temperature), while remained in zone B (i.e., under the influence of only temperature). Vanishing of SP absorption is evidenced in the transmittance spectra, that show values close to the transmittance of a bare BK7 substrate. The optical modifications in the zone A of the samples can be explained according to the basic principle of the EFAD technique: due to the influence of electric field and temperature, electrons from clusters can tunnel to the anode, leaving positively charged silver clusters. Metal ions can be then easily ejected from the cluster, finally resulting in the complete dissolution of the clusters and thus in the absence of SP absorption.



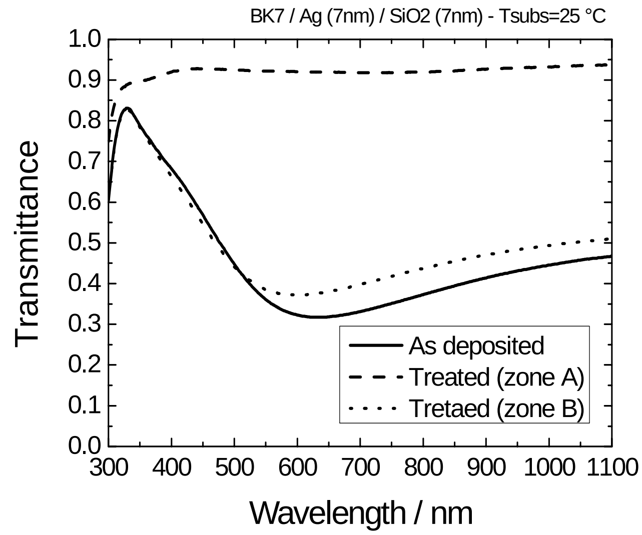
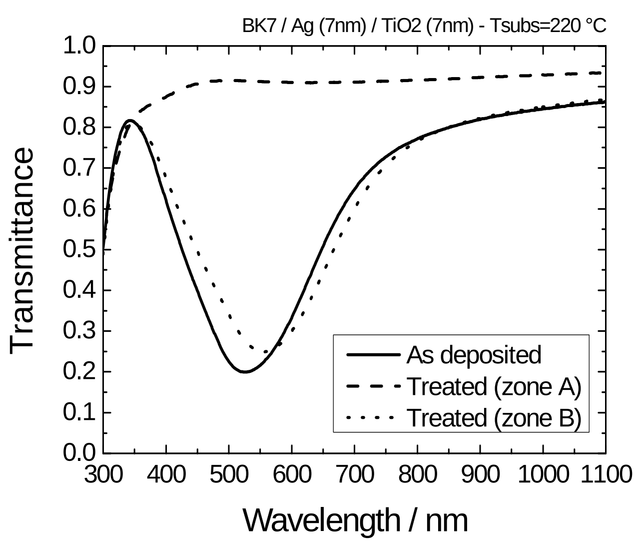


Fig. 5. (left) Transmittance of Ag metal island films coated with SiO_2 and deposited at 220 °C: as deposited (solid line) and zone A after EFAD treatment (dashed line). Fig. 6. (right) Transmittance of Ag metal island films coated with SiO_2 and deposited at 25 °C: as deposited (solid line) and zones A (dashed) and B (dotted) after EFAD treatment.



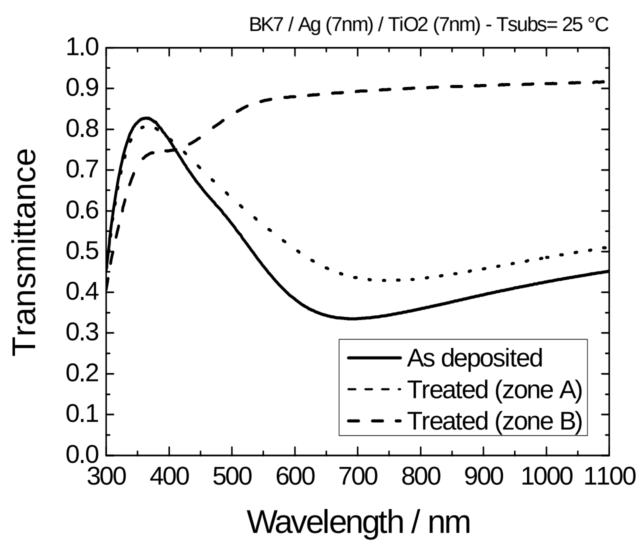


Fig. 7. (left) Transmittance of Ag metal island films coated with TiO_2 and deposited at 220 °C: as deposited (solid line) and zones A (dashed) and B (dotted) after EFAD treatment (dashed line). Fig. 8. (right) Transmittance of Ag metal island films coated with TiO_2 and deposited at 25 °C: as deposited (solid line) and zones A (dashed) and B (dotted) after EFAD treatment.

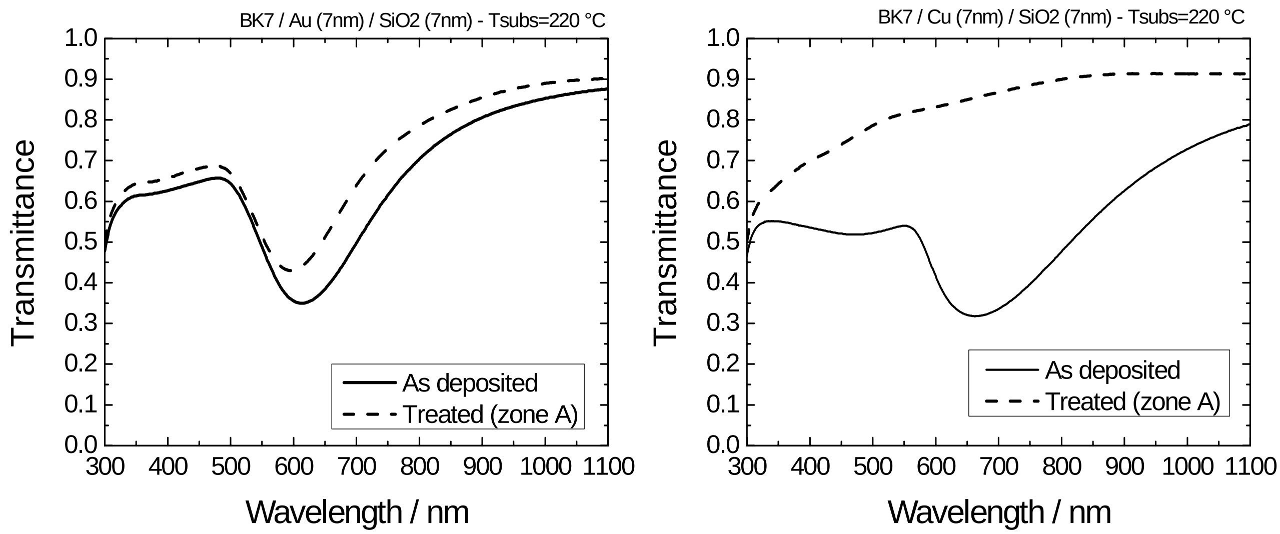


Fig. 9. (left) Transmittance of Au metal island films coated with SiO_2 and deposited at 220 °C: as deposited (solid line) and zone A after EFAD treatment (dashed line). Fig. 10. (right) Transmittance of Cu metal island films coated with SiO_2 and deposited at 220 °C: as deposited (solid line) and zone A (dashed) after EFAD treatment.

The SP absorption completely disappeared for Ag and Cu metal islands films in zone A upon treatment. However, for Au metal island films, the SP resonance only partially vanished, indicating a partial dissolution of clusters. Applying higher electric fields and temperatures leaded to a stronger decrease of the SP absorption. The diversity of results of the bleaching process depending on the clusters material can be associated to the differences in ionization of different metals[10]. A comparison of the standard reduction potential of these metals in liquid solutions (+1.83 V for Au, +0.8 V for Ag and +0.5 V for Cu[10]) gives an idea of the different oxidation likelihood. Since the cluster dissolution starts with the ionization of clusters, higher energies (i.e., higher electric field and/or temperature) have to be supplied in the case of Au island films.

Similarly to the case of glasses containing metal nanoparticles[20], minimum values of electric field and temperature were necessary to perform complete bleaching of the samples, what is related to an ionization threshold of clusters. The experiments showed that these threshold values were not significantly different for different dielectric coatings on MIF or deposition temperatures. In order to obtain homogeneous bleaching of the samples, tight contact between the anode and the sample surface was necessary. In particular, the best results were achieved using as anode a Cr thin film deposited on a glass substrate. If using mechanically polished metal surface as anode, bleaching was not homogeneous due to the local contact imperfections, leading to variations of the effectively applied electric field.

In the zone A of the treated samples, slight interference fringes are seen in these optical spectra, that can be attributed not only to the thin dielectric coating but also to regions of glass with higher concentration of ions that have been drifted from other regions by effect of electric field and temperature, as in thermal poling of glass. Consequently, a small refractive index gradient appears in the substrate[21], giving place to weak interferential effects. Spectra of zones B show a narrower SP absorption with respect to the untreated samples that can be associated to the increase of sphericity of metal clusters upon thermal annealing[17,18].

5. CONCLUSION

The application of metal clusters EFAD in metal island films is demonstrated. The dissolution process has been achieved in samples with different SP properties, due to differences in metallic clusters (Ag, Au, Cu), dielectric material coating the MIF (SiO_2, TiO_2) or the geometry of clusters depending on the deposition temperature. The study shows that EFAD can take place in these two-dimensional systems, what might be valuable for device miniaturization and surface structuring. Overall, the inexpensive requirements of the EFAD technique, in addition to the simple manufacture and high degree of tuning of optical behavior of MIFs, could be used to obtain low-cost and mass-production photonic and plasmonic structures.

REFERENCES

[1] Baba, K., Okuno, T. and Miyagi, M. “Silver-gold compound metal island films prepared by using a two-step evaporation method” App. Phys. Lett. 62(5), 437 (1993).

[2] Xu, G., Tazawa, M., Jin, P., Nakao, S. and Yoshimura, K. “Wavelength tuning of surface plasmon resonance using dielectric layers on silver island films” App. Phys. Lett. 82(22), 3811 (2003)

[3] Gupta, R., Dyer, M. J. and Weimer, W. A. “Preparation and characterization of surface plasmon resonance tunable gold and silver films” J. Appl. Phys. 92(9), 5264. (2002)

[4] Gotschy, W., Vonmetz, K., Leitner, A. and Aussenegg, F. R. “Optical dichroism of lithographically designed silver nanoparticle films” Opt. Lett. 21(15), 1099 (1996)

[5] Lahav, M., Vaskevich, A. and Rubinstein, I. “Biological sensing using transmission surface plasmon resonance spectroscopy” Langmuir, 20(18), 7365 (2004)

[6] Atwatte, H. A. “The promise of Plasmonics” Scientific American, 296(4) (March 2007)

[7] Hassanni, A. and Skorobogatiy, M. “Design of the microstructured optical fiber-based surface plasmon resonance sensors with enhanced microfluidics” Opt. Express, 2006, 14(24), 11616

[8] Podlipensky, A., Abdolvand, A., Seifert, G., Graener, H., Deparis, O. and Kazansky, P. G. “Dissolution of silver nanoparticles in glass through an intense dc electric field” J. Phys. Chem. B 108, 17699 (2004).

[9] Lipovskii, A. A., Melehin, V. and G., Petrikov, V. D. “Electric-field-induced bleaching of ion-exchanged glasses containing copper nanoparticles” Tech. Phys. Lett. 32(3), 275 (2006)

[10] Mezzapesa, F. P., Carvalho, I. C. S., Kazansky, P. G., Deparis, O., Kawazu, M., Sakaguchi, K. “Bleaching of sol-gel glass film with embedded gold nanoparticles by thermal poling” Appl. Phys. Lett. 89(18), 183121 (2006)

[11] Abdolvand, A., Podlipensky, A., Matthias, S., Syrowatka, F., Gösele, U., Seifert, G and Graener, H. “Metallodielectric two-dimensional photonic structures made by electric-field microstructuring of nanocomposite glasses” Adv. Materials, 17, 2983 (2005)

[12] Abdolvand, A., Podlipensky, A., Matthias, S., Syrowatka, F., Seifert, G. and Graener, H. “Silver-doped nanocomposite glass as a base material for fine metallodielectric microstructuring” Proc. SPIE, 6195, 215 (2006)

[13] Sancho-Parramon, J., Janicki, V., Arbiol, J., Zorc, H. and Peiró, F. “Electric field assisted dissolution of metal clusters in metal islands films for photonic heterostructures” Appl. Phys. Lett. 2008, 92, 163108 (2008).

[14] Kreibig, U. and Vollmer, M. “Optical properties of metal clusters”. Springer, Berlin, 1995.

[15] Kelly, K. L., Coronado, E., Zhao, L. L. and Schatz, G. C. “The optical properties of metal nanoparticles: The influence of size, shape and dielectric environment”. J. Phys. Chem. B, 107, 668 (2003).

[16] SOPRA n&k Optical Database

[17] Heger, P., Stenzel, O. and Kaiser, N. “Metal island films for optics” Proc. SPIE 5250, 21 (2004)

[18] Singer, R. R., Leitner, A. and Aussenegg, F. R., “Structure analysis and models for optical constants of discontinuous metallic silver films” J. Opt. Soc. Am. B 12, 22 (1995)

[19] Sancho-Parramon, J., Bosch, S., Abdolvand, A., Podlipensky, A., Seifert, G., and Graener, H. “Effective medium models for metal-dielectric composites: an analysis based on the spectral density theory”. Proc. SPIE 5963, 556 (2005)

[20] Deparis, O., Kazansky, P. G., Podlipensky, A., Abdolvand, A., Seifert, G. and Graener, H. “Evolution of poling-assisted bleaching of metal-doped nanocomposite glass with poling conditions” Appl. Phys. Lett. 86, 261109 (2005)

[21] Brennand A. L. R. and Wilkinson, J. S. “Planar waveguides in multicomponent glasses fabricated by field-driven differential drift of cations” Opt. Lett. 27, 906 (2002)